PB-232 370

CARBONATE BONDING OF TACONITE TALLINGS

Paul J. LaRose, et al

Applied Technology Corporation

Prepared for:

Environmental Protection Agency

January 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the Office of Research and Development, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

EPA-670/2-74-001
January, 1974

CARBONATE BONDING OF TACONITE TAILINGS

By

Paul J. LaRosa, K. A. Ricciardella
and
R. J. McGarvey

Contract No. 68-01-0195
Program Element No. 1BB040

Project Officer
Ronald D. Hill
Mining Pollution Control Branch
National Environmental Research Center
Cincinnati, Ohio 45268

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
Washington, D. C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1

ABSTRACT

The carbonate bonding process consists of mixing a suitable material with water and lime hydrate, compacting the mixture, and reacting it with carbon dioxide-rich gas to form a coherent structure bonded by a matrix of calcite crystals. A laboratory study has indicated that taconite tailings could be carbonate bonded to form an effective road paving or brick-making material. In general, the compressive strength of carbonate bonded taconite tailings increased with increasing lime hydrate content, reaction time, and carbon dioxide concentration in the reaction gas. In addition, air and water permeabilities, freeze-thaw resistance, and flexural strengths of carbonate bonded taconite tailings were found to be comparable to concrete. Scale-up of the laboratory studies to demonstrate paving applications in small plots was hampered by a failure to obtain sufficient compaction. The results, however, did confirm the laboratory study findings.

Possible applications of the carbonate bonding process utilizing taconite tailings are road building, formation of aggregate, and brickmaking. An approximate cost comparison suggests that the road construction application is an economical alternative to conventional road building materials and techniques.

This report was submitted in fulfillment of Contract No. 68-01-0195 by Applied Technology Corporation under sponsorship of the Environmental Protection Agency. Work was completed as of December, 1973.

CONTENTS

	Page
Abstract	ii
List of Figures	iv
List of Tables	v
Acknowledgements	vi
SECTIONS	
I Conclusions	1
II Recommendations	3
III Introduction	5
IV Experimental Studies (Briquettes)	7
Raw Materials Used	7
Carbonate Bonding Technique and Apparatus	8
Experimental Program	10
Effect of Lime Hydrate on Compressive Strength	10
Effect of Water Content on Compressive Strength	11
Effect of Curing Time on Compressive Strength	12
Effect of Carbon Dioxide Concentration on Compressive Strength	15
Effect of Formation Load on Compressive Strength	17
Lime Hydrate Study	17
Air and Water Permeability of Carbonate Bonded Taconite Tailings	21
Freeze-Thaw Test on Carbonate Bonded Taconite Tailings	22
Flextural Strength Tests on Carbonate Bonded Taconite Tailings	24
Subsequent Experimentation	24
V Experimental Study (Bricks)	25
Carbonate Bonding of Taconite Tailings as 15 cm Cubes	25
VI Taconite Test Plots	30
VII Application of Carbonate Bonded Taconite Tailings	38
Process Description	38
Suggested Operating Parameters	39
Process Economics	40
VIII Appendices	43
Theoretical Consideration of Carbonate Bonding	43
Determination of Air Permeability	47
Determination of Water Permeability	51
Freeze-Thaw Test	53

FIGURES

Page

1. Carbonate Bonding Reaction System. 9
2. Effect of Lime Hydrate Content on Compressive Strength . . . 11
3. Effect of Moisture Content on Compressive Strength Using 15 Weight Percent Lime Hydrate 12
4. Effect of Moisture Content on Compressive Strength Using 20 Weight Percent Lime Hydrate 13
5. Effect of Curing Time on Compressive Strength. 14
6. Reduced Compressive Strength vs Curing Time. 15
7. Effect of Carbon Dioxide Concentration on Compressive Strength 16
8. Effect of Reaction Time on Compressive Strength. 16
9. Effect of Formation Load on Briquette Compressive Strength . 17
10. Effect of Lime External Surface Area on Compressive Strength 20
11. Compressive Strength vs Freeze-Thaw Cycles 23
12. Sectioned Bricks Reacted with 100 Percent CO_2. 26
13. Sectioned Bricks Reacted with 20 Percent CO_2 26
14. Carbonate Bonded Depth vs Time for 15 cm Bricks. 27
15. Effect of Formation Load on Depth of Carbonate Bonding of 15 cm Bricks 29
16. Configurations of Plots 1 and 2. 31
17. Configuration of Plots 3, 4, and 5 32
18. Location of Sampling Sites in Each Test Plots. 34
19. Compressive Strength vs Density for Plots 3, 4, and 5. . . . 36
20. Carbonate Bonding Model. 46
21. Air Permeability Apparatus 48
22. Water Permeability Apparatus 52

TABLES

		Page
1	Screen Analysis of Taconite Tailings	7
2	Chemical and Screen Analysis of Lime Hydrates Tested	7
3	Compressive Strength of the Lime Hydrate Briquettes (dry CO_2)	18
4	Compressive Strength of the Lime Hydrate Briquettes (wet CO_2)	19
5	Air Permeability of Taconite Tailings Briquettes	21
6	Water Permeability of Taconite Tailings Briquettes	22
7	Plot Thickness	30
8	Plot CO_2 Addition Rate	33
9	Test Results for Plots 3, 4, and 5	35
10	Paving Cost	40
11	Paving Cost for Carbonate Bonding	41
12	Paving Cost	41

ACKNOWLEDGEMENTS

The support of the project by the Environmental Protection Agency and the help provided by Dr. James M. Schackelford and Mr. Ronald D. Hill, Project Officers, is acknowledged with sincere thanks.

SECTION I

CONCLUSIONS

Carbonate bonding consists of mixing a material with water and lime hydrate, compacting the mixture, and reacting it with carbon dioxide-rich gas to form coherent structures bonded by a matrix of calcite crystals. This study has shown that taconite tailings can be used in the carbonate bonding process. To minimize pollution of Lake Superior by taconite tailings, the taconite can be carbonate bonded rather than stockpiled and utilized as a road building material, road aggregate, and/or in the preparation of bricks.

The following conclusions have resulted from this study:

1. In the laboratory, compressive strengths in the order of 281 kg/cm^2 (4000 psi) were obtained from carbonate bonded taconite tailings. For these studies, taconite tailings containing 3 to 5 percent moisture were mixed with 20 percent lime hydrate and reacted with carbon dioxide-rich gas. The compressive strength of the carbonate bonded taconite tailings increased with increasing lime hydrate content, formation load, carbonate bonding reaction time, and carbon dioxide concentration of the reaction gas.

2. Air and water permeabilities of carbonate bonded taconite tailings were found to be comparable to those of concrete.

3. A lime hydrate study indicated that dolomitic lime hydrates with high external surface areas yield the highest compressive strengths.

4. A simplified model of carbonate bonding was developed and indicated that the progression of the carbonate bonding interface is related to the square root of time. A brick study (15 cm cubes) confirmed the model and yielded compressive strengths for the bricks in the order of 225 kg/cm^2 (3200 psi). Although no economics were generated, it appears that taconite tailings could be utilized in the preparation of bricks.

5. A plot study involving the carbonate bonding of several 1.2 metre (4 ft) squares was hampered by inclement weather and insufficient compaction. The results agreed with smaller scale study work and indicated that a single source of carbon dioxide at the center could carbonate bond a 1.2 metre (4 ft) square. However, due to uneven compaction resulting from roller/plot size limitations, the compressive strength of the plot decreased at locations away from the center of

the plot. Further work is required to develop adequate techniques to control carbon dioxide injection, moisture content of taconite tailings, and uniform compaction before this process can be utilized for road paving applications.

6. If the adequate paving techniques mentioned above do not result in increased labor or equipment costs over conventional paving techniques, an approximate cost comparison indicates that carbonate bonded taconite tailings are comparable, and in some cases, less costly than conventional road construction materials. For secondary road construction, an 8-inch layer of carbonate bonded taconite tailings would cost approximately $11.31 per square yard, as compared to $11.50 per square yard for a comparable bituminous pavement with base course. In the construction of first class roads, carbonate bonding offers a cost saving of approximately $2 per square yard as compared to concrete.

7. Based on the above economic comparison and the results of the laboratory study, there could be an incentive to utilize the carbonate bonding process to minimize stockpiling of taconite tailings and reduce its harmful ecological effects.

SECTION II

RECOMMENDATIONS

Because of the encouraging results of this study, ATC believes that additional carbonate bonding development work is warrented. Such work must be conducted on a larger scale under more controlled conditions. It is recommended that the following demonstration studies be conducted in the following sequence:

1. A study should be conducted to ascertain the techniques and economics of brick preparation using taconite tailings. This study would include some basic experimentation but would be more orientated toward preparing preliminary specifications for a brick making facility. This application may be of particular interest to U. S. AID programs in developing countries.

2. A study should be conducted to determine how moisture content, carbon dioxide injection, and compaction can be controlled under field conditions for road paving applications.

3. It is recommended that a large plot be paved to develop adequate techniques and to demonstrate the commercial utility of the process as a road building technique. For demonstration purposes, the test plot should be a minimum of 6 m by 15 m (20 ft x 50 ft) to permit the utilization of commercial-sized compaction equipment. Based on the results from the demonstration plot, an engineering evaluation of the process would be made with pertinent recommendations as to further application.

4. If items 2 and 3 are successful, it is recommended that the process be demonstrated by construction of a secondary road in the vicinity of a taconite tailings pile. This demonstration would reduce the size of the selected taconite tailings pile, provide additional roads for the community, establish road building costs, and develop road building techniques for application of the carbonate bonding process.

5. A study should be conducted to determine the technical and economic feasibility of manufacturing aggregate using carbonate bonding taconite tailings. This aggregate may have applications in road or building construction.

6. As part of any of the above projects, a study should be undertaken to determine the feasibility of producing lime hydrate suitable for carbonate bonding from limestone available near taconite tailings sources. The purpose of this work would be to minimize the cost of transporting lime hydrate to the point of use.

ATC strongly recommends the brick study (1) above, because it believes that this application of the process can be implemented in a relatively short period of time with a minimum of development work. Brick manufacturing equipment should be relatively simple, employing a brick press, standard drying and mixing equipment, a carbonate bonding chamber, and CO_2 gas generator.

SECTION III

INTRODUCTION

The Lake Superior District is a major source of iron ore for the United States. The ores mined in this region vary widely in mineralogy, chemical composition, and marketability. Prior to 1950, mining was restricted to marketable lump or easily beneficiated ores. However, as reserves dwindled, attention was focused on the recovery of iron from low grade taconite in the 1950's. Despite their low iron content (25 to 35 percent total iron as mined), taconite ores could be beneficiated to increase the iron content and produce a high quality blast furnace feed.

Taconite is a hard, dense, fine grain rock that normally contains about 40 to 55 percent silica. To produce an acceptable iron ore concentrate, the silica must be removed prior to shipment. Typically this is accomplished by grinding the taconite ore to 200 mesh or finer and then separating the tailings from the iron oxide by magnetic separation or flotation techniques. These tailings or gangue produced in the beneficiation process are extremely fine and represent a source of water pollution. The finely sized tailings which enter Lake Superior either through the discharge of process water or storm water run-off, remains in suspension for extended periods of time. This brings about an upset in the natural environment of the lake. The taconite tailings being finely sized, hard, and sharp edged cause multiple minute abrasions on the interior and exterior of fish or similar aquatic life. Additionally, the huge surface area of the finely sized particles tend to enhance the solution of trace elements which may induce undesirable side chemical reactions. The esthetic appearance of the lake is also destroyed because of the cloudy haze created by the particles held in suspension. For these reasons, methods are being sought to utilize taconite tailings and, thereby, prevent or minimize this serious form of water pollution.

This study involves the investigation of a process in which taconite tailings can be profitably transformed into a concrete like material. This material can be used as a filler in the construction of carbonate bonded road pavement and in the manufacture of low-cost bricks and similar products. If successful, there would be sufficient incentive to utilize the taconite tailings and not permit run-off to Lake Superior.

In this process, lime hydrate is blended with taconite tailings and water and then reacted with carbon dioxide to form strong calcium carbonate (calcite) crystals. The calcite crystals act as a cementing matrix that turn the taconite tailings into a coherent and impervious structure. The carbonate bonding process relies on the simple reaction that occurs between carbon dioxide and lime hydrate:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

This reaction is well known and occurs naturally upon the exposure of lime hydrate to the atmosphere. However, the rate of conversion of lime hydrate to calcium carbonate is relatively slow because of the small percentage of carbon dioxide contained in the atmosphere. Although the reaction in air is slow, the reaction proceeds rapidly in concentrated carbon dioxide. Because of their high strength, calcite crystals afford an opportunity for employing lime hydrate as a cementing material to bind taconite tailings into a coherent structure. A more detailed description of carbonate bonding can be found in the Appendix.

The majority of experimentation prior to this work has been conducted using coal refuse rather than taconite tailings as the filler material. (For reference see EPA report entitled, "Carbonate Bonding of Coal Refuse", 14010 FOA 02/71.)

This present study was undertaken to determine the operating parameters for generating a strong carbonate bonded taconite tailings structure and to determine the feasibility of the carbonate bonding process for the paving of roads. In particular, the effects of different brands of lime hydrate with varying lime hydrate contents, moisture content, partial pressure of carbon dioxide in the carbonating gas and carbonation (reaction) time were determined. In addition, air and water permeability, freeze-thaw resistance, and flexural strength tests were determined for carbonate bonded taconite tailings.

SECTION IV

EXPERIMENTAL STUDY (BRIQUETTES)

RAW MATERIALS USED

Fine taconite tailings were obtained from the Reserve Mining Company*, Silver Bay, Minnesota. The screen analysis for these taconite tailings is presented in Table 1.

Table 1
Screen Analysis of Taconite Tailings

Mesh	Cumulative Weight, %
10	96.7
20	89.0
35	79.6
65	68.2
100	61.8
200	43.6
325	30.5
500	24.1

The external surface area of the taconite tailings was determined using an air permeability technique in which the Carman-Kozeny equation was used to relate the external surface area to the pressure drop of air passing through a packed bed of taconite tailings. This procedure is presented in detail in the Appendix. The average external surface area of the taconite tailings was determined to be 552.4 cm^2/gram. Table 2 shows the chemical analysis and screen analysis of the lime hydrates tested in this study. Initial experiments were performed using Ohio Super Spray* while latter experiments were performed to investigate the effects of the various lime hydrates of Table 2 on carbonate bonding properties.

Table 2
Chemical and Screen Analysis of Lime Hydrates Tested

Sample	Manufacturer	Chemical Analysis		
		CaO	MgO	$Ca(OH)_2$
Pfizer Spray	Pfizer Co.	43.82%	31.03%	36.86%
Tiger Finish	Pfizer Co.	42.15%	29.19%	37.82%
National Hydrate	National Lime & Stone Co.	48.19%	33.82%	49.86%
Mercer Lime	Mercer Lime & Stone Co.	73.63%	0.61%	96.07%
Marble Cliff	Sciota Lime & Stone Co.	70.00%	5.00%	92.00%
Ohio Super Spray	Ohio Lime Co.	49.20%	34.00%	65.00%

*Mention of trade names does not imply endorsement nor recommendation by either Applied Technology Corporation or the Environmental Protection Agency

Table 2 Continued

Sample	U.S. Mesh Percent/Passing 100 Mesh	200 Mesh	325 Mesh	External Surface Area $cm^2/gram$
Pfizer	100.00%	90.86%	54.13%	5432
Tiger Finish	100.00%	85.85%	54.86%	4659
National Hydrate	100.00%	98.84%	85.39%	6404
Mercer Lime	100.00%	99.91%	99.21%	2492
Marble Cliff	99.50%	94.00%	63.45%	5698
Ohio Super Spray	100.00%	99.78%	99.64%	5330

CARBONATE BONDING TECHNIQUE AND APPARATUS

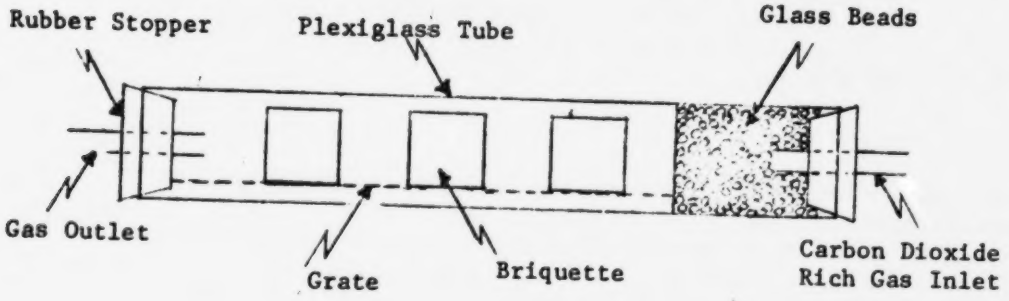
The preparation of taconite tailings for carbonate bonding consisted of mixing in sufficient water to bring the water content to a specified value. This mixture was allowed to stand to permit an equilibration of water throughout the mixture. Lime hydrate was then thoroughly blended into the taconite tailings. To permit a rapid scanning of parameters and to minimize the quantities of materials and size of the carbonate bonding apparatus, the lime hydrate-taconite tailings mixture was placed in a small die and compacted to yield briquettes 5 cm diameter by 5 cm high. Compaction loads varying from 35 kg/cm^2 to 281 kg/cm^2 (500-4000 psi) were used to form the briquettes of these experiments. In the commercial application of the carbonate bonding process, lower compaction loads in the order of 70 kg/cm^2 (1000 psi) would be used. It was decided to use higher compaction load for experimental purposes so that the briquettes would not have loose edges and would be of exact dimensions. The briquetting pressure was then removed and the soft, easily crushed briquette was placed in a reactor and contacted with a carbon dioxide-rich gas for a specified time.

The carbonate bonding reactor is shown schematically in Figure 1. Tanks of carbon dioxide and nitrogen were used as the source of the carbonating gas constituents. Experiments were run with carbonate bonding gas containing 15 to 100 percent carbon dioxide concentrations. The carbon dioxide and nitrogen were individually metered, combined in a mixing chamber, and admitted to the carbonate bonding reactor. The reactor consisted of a plexi-glass tube, 9.52 cm I.D. by 61 cm long (3.75 x 24 inches). The formed briquettes were placed on a metal grate which slid into the reactor tube. Six reactor tubes were used to react several batches of briquettes in a single operation.

To carbonate bond the briquettes they were placed in the reactor tubes. The flow rates of nitrogen and carbon dioxide were then adjusted to the desired flows. During this initial adjustment, the flow of the gas mixture bypassed the reactor tubes. Once the desired gas mixture was obtained, a stopwatch was started and the bypass valve closed causing the gas mixture to enter the reactor tubes.

When the specified carbonate bonding reaction time was reached, the carbon dioxide was cut off and nitrogen was allowed to flow through the

Reproduced from best available copy.



Reactor System

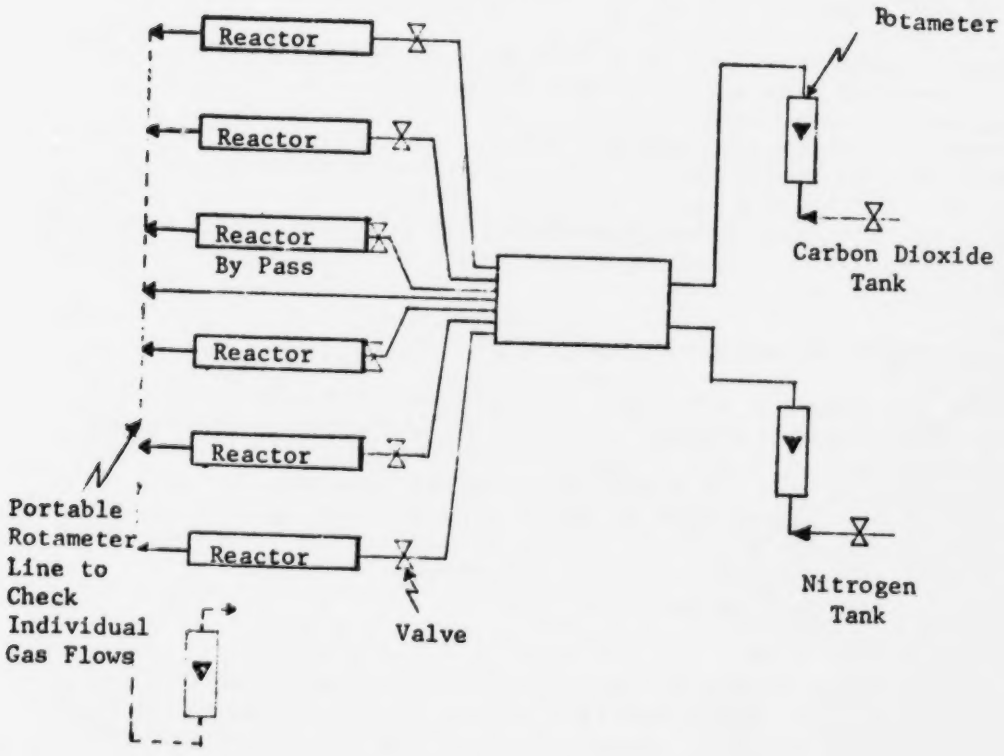


FIGURE 1. CARBONATE BONDING REACTOR SYSTEM

reactor tubes for several additional minutes to flush out all remaining reaction gas. The carbonate bonded taconite tailings briquettes thus formed were removed and either tested for their compressive strength or subjected to other tests.

EXPERIMENTAL PROGRAM

The structural integrity of carbonate bonded taconite tailings is a prime consideration for any of its possible applications. Since the process is being investigated as a possible road pavement, the compacted layer must have sufficient strength to withstand heavy vehicular traffic. Consequently, in this study, it was necessary to select one strength property as representative of the structural integrity of the resulting carbonate bonding material. For this study, compressive strength was selected because of its applicability toward the intended use of the carbonate bonding process and because of its ease of determination. To determine the compressive strength of carbonate bonded briquettes, a briquette was placed in a press and the press plates closed until a small load was applied to the briquette. The press operator then applied a slow but continuous rate of loading on the briquette until failure occurred. The load at failure was recorded and used to calculate the compressive strength of the briquette.

The laboratory experimentation can be divided into two categories: those experiments designed to investigate the effects of various carbonate bonding parameters (lime hydrate content, moisture content, etc.) on the compressive strength and those experiments which were used to determine the physico-chemical properties of carbonate bonded taconite tailings. Initially, Ohio Super Spray lime hydrate was used to prepare the carbonate bonded taconite tailings. Prior experimentation with coal refuse suggested that this lime hydrate would be suitable. Later in the experimental program other lime hydrates were tested.

EFFECT OF LIME HYDRATE CONTENT ON COMPRESSIVE STRENGTH

To determine the effect of lime hydrate content on briquette compressive strength, briquettes were prepared in which the lime hydrate content was varied between 5 and 20 weight percent. The water content was held constant at 3 weight percent for these tests. After blending, the taconite-lime hydrate mixture was charged to the five cm diameter mold and compressed at 84 kg/cm^2 (1200 psi) to yield a 5 cm high cylindrical briquette. The briquettes were then reacted for six hours using pure carbon dioxide, removed from the reactor and subjected immediately to a compressive strength determination.

The results are shown in Figure 2 where the briquette compressive strength is shown as a function of lime hydrate content. Figure 2 clearly indicates that the compressive strength increases as the lime content is increased.

PB 232 370

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. | 2. | 3. Accession No. W 74-07959

4. Title

CARBONATE BONDING OF TACONITE TAILINGS,

5. Report Date

6.

8. Performing Organization Report No.

7. Author(s)

LaRosa, Paul J., Ricciardella, Kenneth A., McGarvey, Ronald J.

10. Project No. EPA Program Element 1BB040

9. Organization

Applied Technology
~~135 Delta Drive~~
Pittsburgh, PA. ~~15238~~

11. Contract/Grant No.

68-01-0195

12. Type of Report and Period Covered

~~12. Sponsoring Organization U.S. Environmental Protection Agency~~

15. Supplementary Notes

Environmental Protection Agency, Technology Series report ~~number~~ EPA-670/2-74-001, January, 1974. 53p, 22 fig, 12 tab,

16. Abstract

Carbonate bonding consists of mixing and compacting a suitable material with water and lime hydrate, and then reacting it with a carbon dioxide-rich gas to form a coherent structure bonded by a matrix of calcite crystals. Carbonate bonding of mining refuse can minimize the pollution associated with refuse stockpiling and disposal.

A laboratory study has indicated that taconite tailings can be carbonate bonded to form an effective road paving or brick-making material. In general, the compressive strength of carbonate bonded taconite tailings increased with increasing lime hydrate content, reaction time, and carbon dioxide concentration in the reaction gas. Air and water permeability, freeze-thaw resistance, and flexural strength of carbonate bonded taconite tailings were found to be comparable to concrete. Scale-up of the laboratory studies to demonstrate paving applications in small plots was hampered by a failure to obtain sufficient compaction. The results, however, did confirm the laboratory study findings.

Possible applications of the carbonate bonding process utilizing taconite tailings are road building, formation of aggregate, and brickmaking. An approximate cost comparison suggests that the road construction application is an economical alternative to conventional road building materials and techniques. (EPA)

17a. Descriptors

Carbonate Bonding, ~~*Taconite Tailings*~~, ~~*Brickmaking*~~, *Road Construction*, Pollution Abatement*, *Aggregates*,

17b. Identifiers

Carbonate Bonding, *Taconite Tailings*, Brickmaking

17c. COWRR Field & Group 056,

Copy Available from GPO Sup Doc as EP1.23:670/2-74-001, $ 1.45 ; microfiche from NTIS as PB-232 370 $1.45

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor P. J. LaRosa

Institution Applied Technology Corporation, Pgh., PA

WRSIC 102 (REV. JUNE 1971)

GPO 913.281

*U.S. GOVERNMENT PRINTING OFFICE:1974 546-316/260 1-3

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

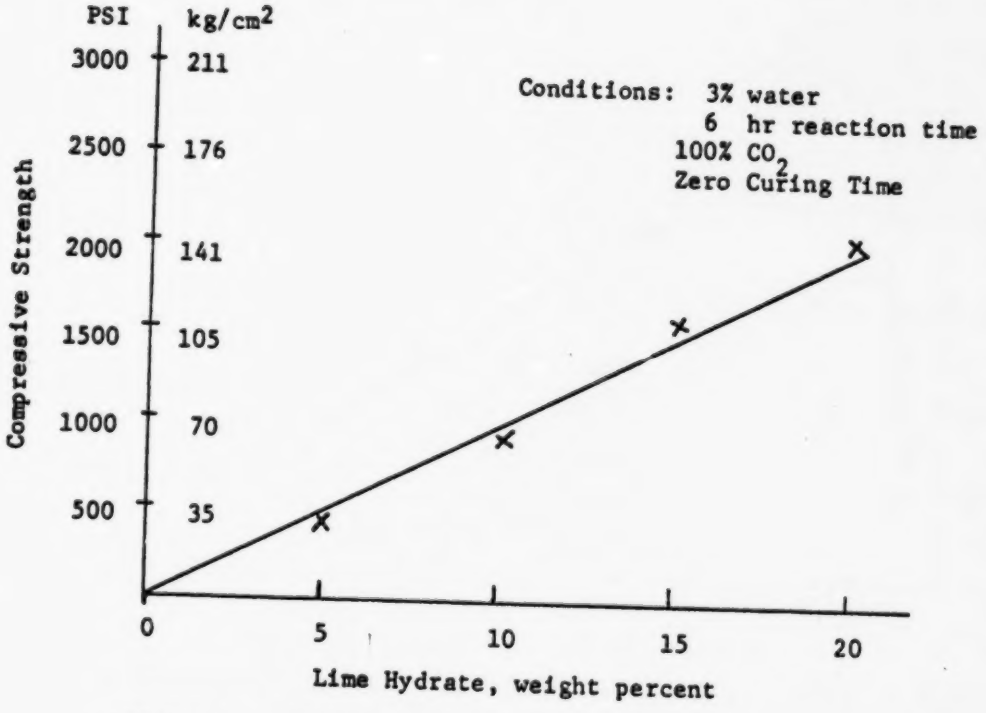


FIGURE 2--EFFECT OF LIME HYDRATE CONTENT ON COMPRESSIVE STRENGTH

The increase in compressive strength with lime hydrate content is expected since more lime hydrate is available for bonding. However, briquettes made with 40 percent lime hydrate developed cracks and had essentially no compressive strength. These cracks developed because the carbonate bonding reaction is highly exothermic. This exothermic reaction causes rapid vaporization of moisture which creates high internal pressure and cracks the briquettes. Consequently, there is a practical limit to the lime hydrate content that can be used effectively to increase the strength of carbonate bonded taconite tailings.

This initial test established that subsequent testing would be done using either 15 or 20 weight percent lime hydrate.

EFFECT OF WATER CONTENT ON COMPRESSIVE STRENGTH

The effect of water content on carbonate bonded compressive strength is shown in Figures 3 and 4. In these experiments, (Figure 3), the taconite

tailings contained 15 percent lime hydrate and a formation load of 70 kg/cm^2 (1000 psi) was used. The briquettes were reacted for six hours and then cured for 100 hours. The maximum compressive strength was achieved at 3 percent moisture as is seen in Figure 3.

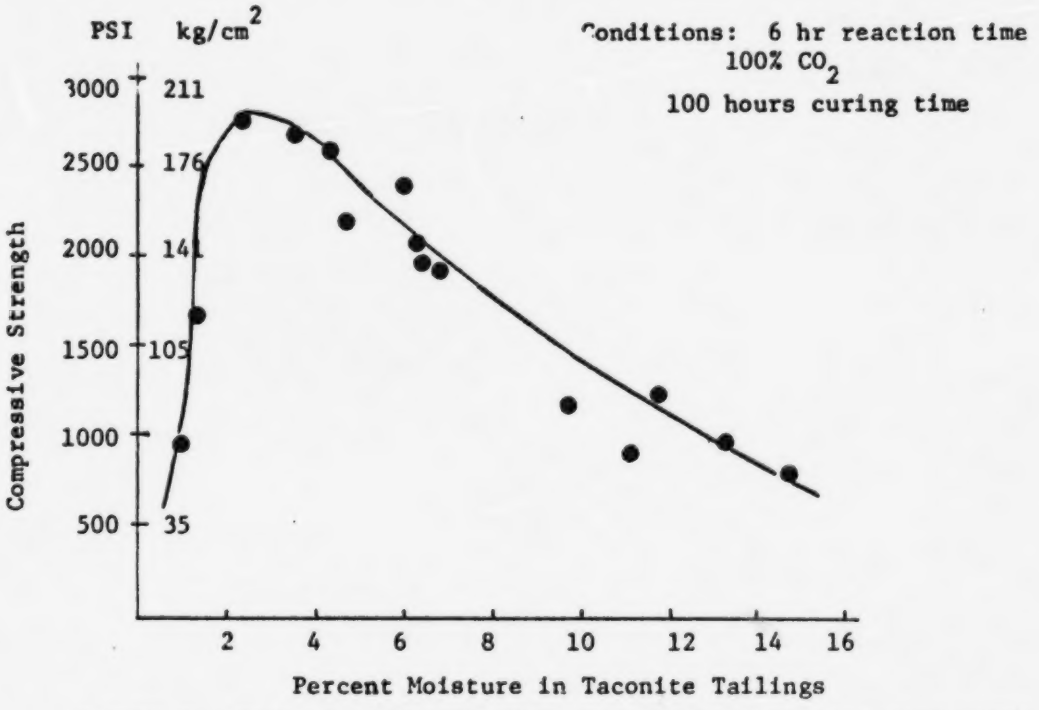


FIGURE 3--EFFECT OF MOISTURE CONTENT ON COMPRESSIVE STRENGTH USING 15 WEIGHT PERCENT LIME HYDRATE

Additional experiments were done using 20 percent lime hydrate, 70 kg/cm^2 formation load, six hour reaction time, and 100 hour curing time. These experiments using 20 percent lime hydrate are shown in Figure 4. As seen, a maximum compressive strength of 211 kg/cm^2 (3000 psi) was achieved at 3 to 5 percent moisture. At a moisture content greater than 5 percent, the compressive strength dropped sharply.

Based on these results, the optimum compressive strength is obtained with 3 to 5 percent moisture. The significance of this result is that since the taconite tailings are produced using a flotation process, they must be dried to a 3 to 5 percent moisture before they can be used in the carbonate bonding process.

EFFECT OF CURING TIME ON COMPRESSIVE STRENGTH

As shown in Figures 3 and 4, the maximum compressive strength obtained for the taconite tailings briquettes was 197 to 211 kg/cm^2 (2800-3000 psi) with 20 percent lime hydrate and 3 to 5 percent water. The resulting

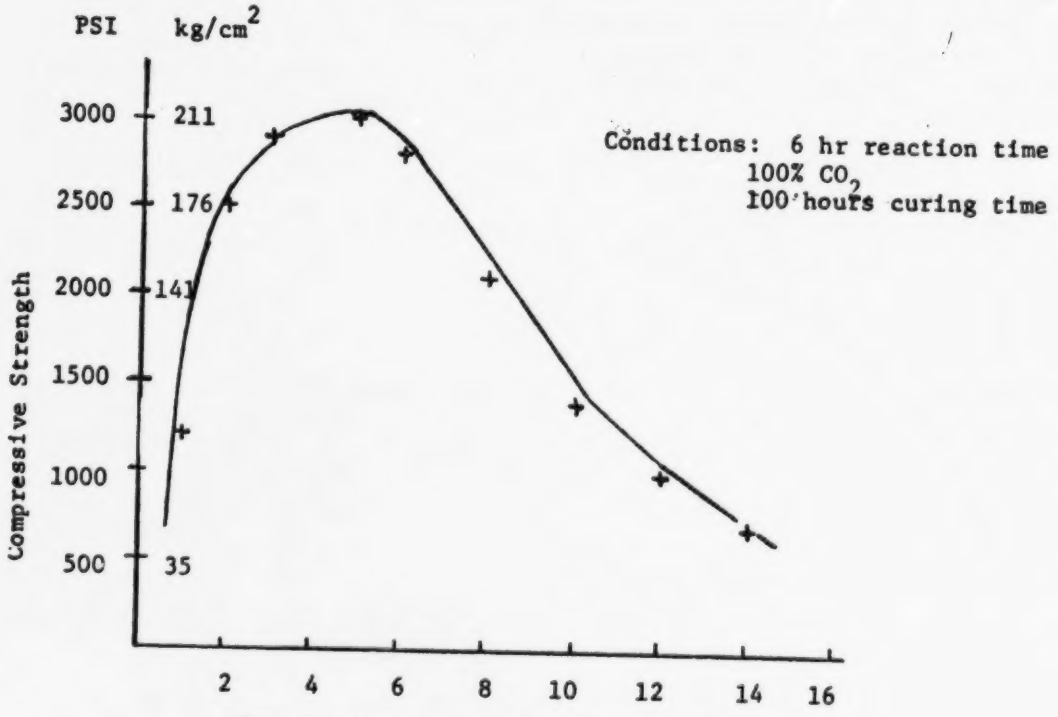


FIGURE 4--EFFECT OF MOISTURE CONTENT ON COMPRESSIVE STRENGTH USING 20 WEIGHT PERCENT LIME HYDRATE

compressive strengths were lower when compared with prior experimental results using other fill materials (coal refuse). Carbonate bonded coal refuse yielded compressive strengths in the order of 281 kg/cm^2. Consequently, experiments were conducted to determine if there is a curing time effect on compressive strength.

To determine the effect of curing time on compressive strength, carbonate bonded briquettes were prepared in the manner described previously except that following reaction with carbon dioxide, the briquettes were permitted to cure at room temperature in the laboratory, for periods up to 700 hours. The compressive strength was then determined as a function of the time elapsed after carbonate bonding was completed. This was done using taconite tailings with 3 percent moisture and 20 percent lime hydrate.

For these experiments, 100 percent carbon dioxide gas was reacted with the briquettes for six hours. Compressive strengths were determined at various times after carbonate bonding was completed up to a total time of 700 hours. In Figure 5 the compressive strength is shown as a function of curing time.

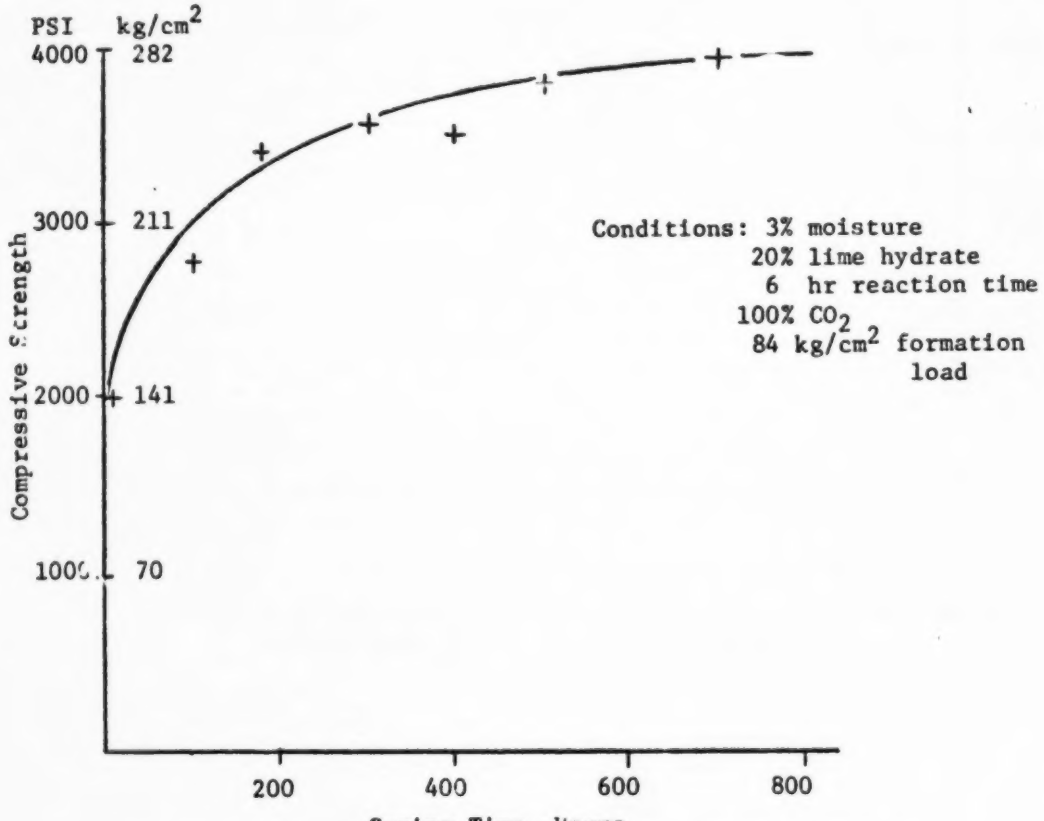


FIGURE 5--EFFECT OF CURING TIME ON COMPRESSIVE STRENGTH

The compressive strength increased significantly during the first 300 hours and continued to gradually increase to a relatively constant value after 700 hours. The taconite tailings compressive strength increased from approximately 239 kg/cm^2 (3400 psi) after 190 hours to 274 kg/cm^2 (3900 psi) after 700 hours.

In order to make these findings generally applicable (as will be shown later), Figure 6 was prepared. Figure 6 is a plot of the reduced compressive strength, as a function of the curing time. The reduced compressive

strength is defined as S/S_f where S = compressive strength at any time, and S_f = compressive strength at steady state conditions (700 hours).

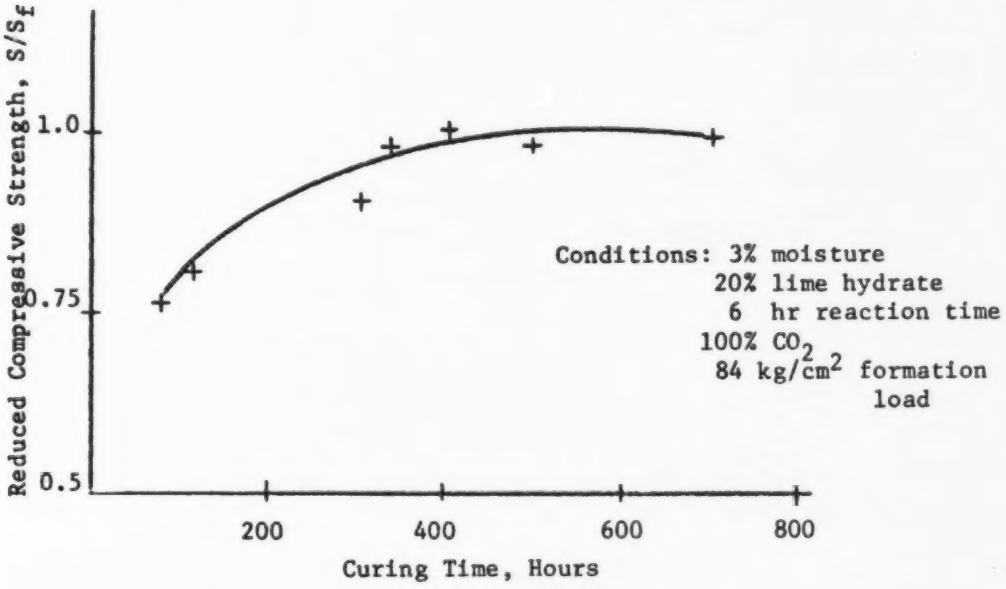


FIGURE 6--REDUCED COMPRESSIVE STRENGTH VS. CURING TIME

EFFECT OF CARBON DIOXIDE CONCENTRATION ON COMPRESSIVE STRENGTH

To determine the effect of carbon dioxide concentration on compressive strength, five separate experiments were conducted using a 15, 30, 50, 70, and 100 percent carbon dioxide-nitrogen gas mixture. Sets of briquettes (20 percent lime hydrate, 3 percent moisture, 70 kg/cm^2 [1000 psi] formation load) were reacted for six hours with varying percents of carbon dioxide. Each set of briquettes was allowed to cure for 190 hours before compressive strengths were determined. Figure 7 shows the effect of carbon dioxide content on briquette compressive strength. The compressive strengths ranged from approximately 169 to 211 kg/cm^2 (2400-3000 psi) for 15 and 100 percent carbon dioxide in the reaction gas, respectively. The lower compressive strength obtained at the 15 percent carbon dioxide level can be compensated for by increasing the carbonate bonding reaction time. The effect of reaction time on compressive strength is shown in Figure 8 for a reaction gas containing 15 percent carbon dioxide. Compressive strengths were determined at intervals of five hours. For a ten hour reaction time, the briquette compressive strength obtained using a 15 percent carbon dioxide reaction gas is comparable to the strength achieved using a six hour reaction time and 100 percent carbon dioxide gas.

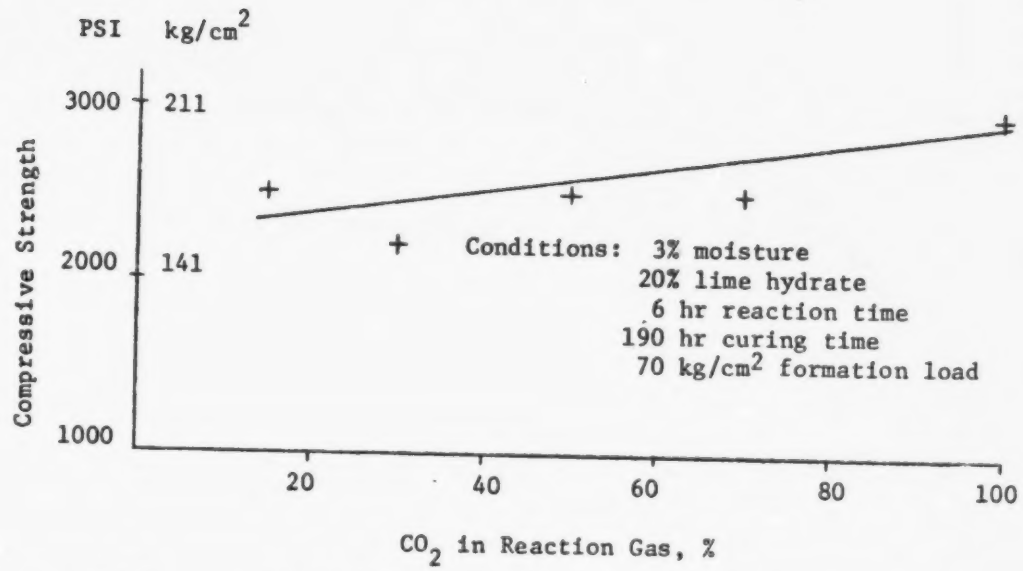


FIGURE 7--EFFECT OF CARBON DIOXIDE CONCENTRATION ON COMPRESSIVE STRENGTH

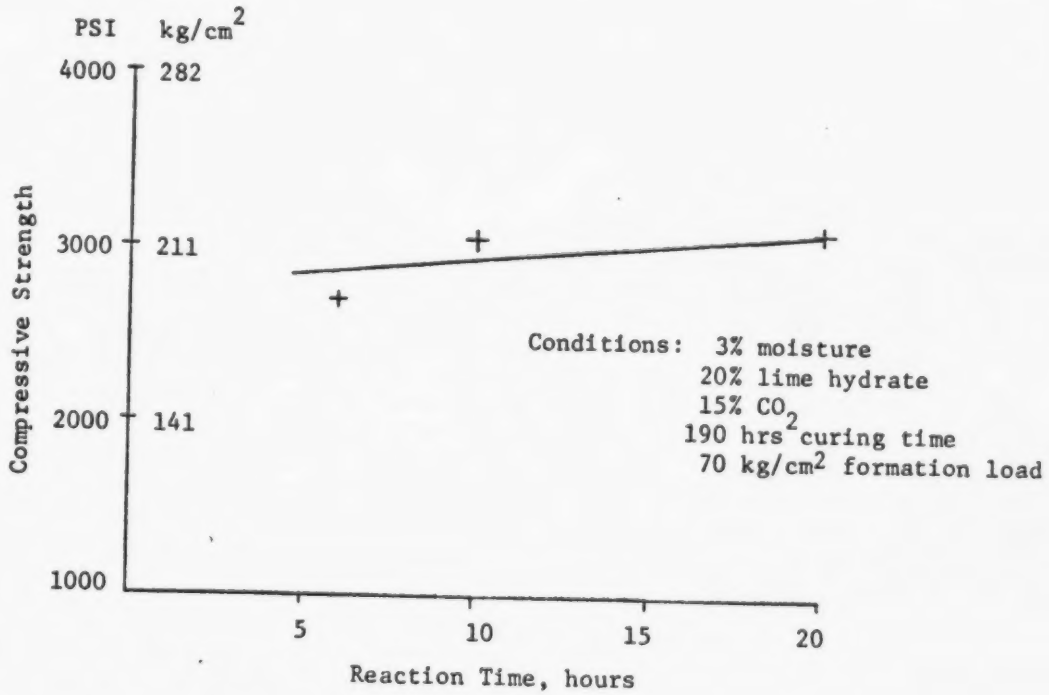


FIGURE 8--EFFECT OF REACTION TIME ON COMPRESSIVE STRENGTH

EFFECT OF FORMATION LOAD ON COMPRESSIVE STRENGTH

Formation load is an important factor in the carbonate bonding of taconite tailings. A study was conducted to determine the effect of the initial formation load (the load applied during briquette preparation) on briquette compressive strength. Briquettes were formed at 35, 70, 140, and 281 kg/cm^2, and reacted with 100 percent carbon dioxide gas for six hours and cured for 190 hours. Figure 9 shows that briquette compressive strength increased from 140 to 323 kg/cm^2 as the formation load was increased from 35 to 281 kg/cm^2. It is, therefore, advantageous to compact the lime hydrate-taconite tailings mixture to as high a degree as possible. Formation loads of 70 to 141 kg/cm^2 (1000-2000 psi) are possible using commercially available equipment.

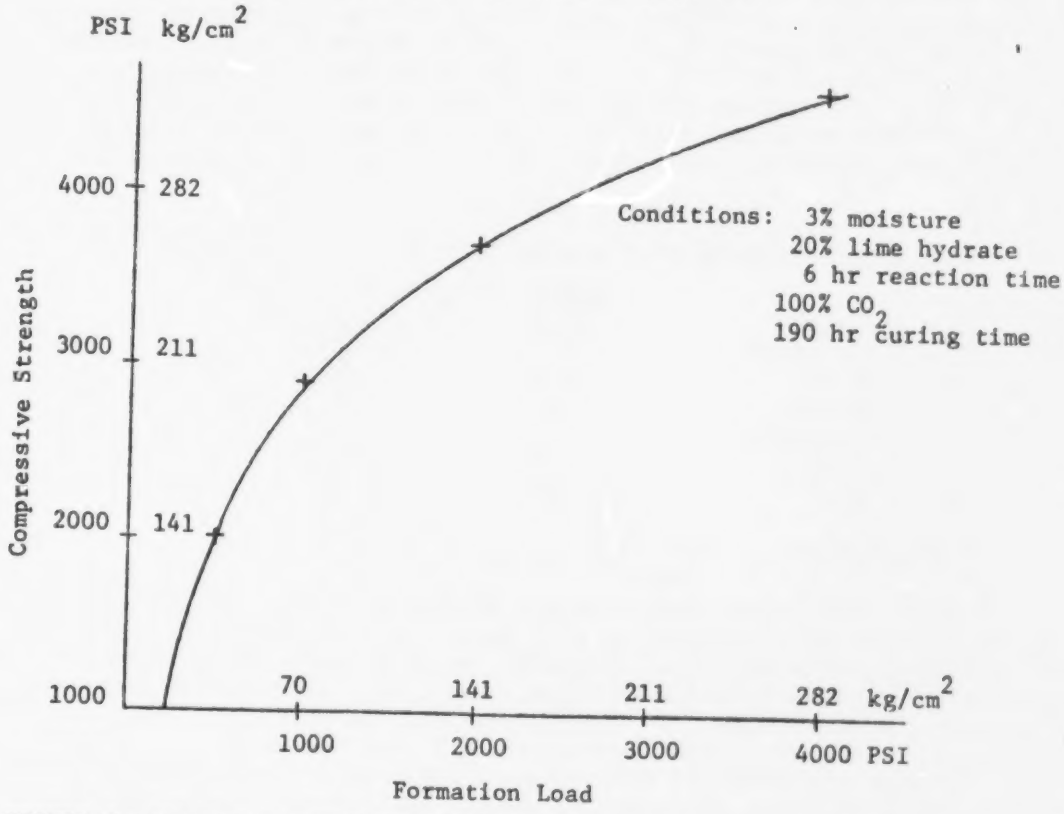


FIGURE 9--EFFECT OF FORMATION LOAD ON BRIQUETTE COMPRESSIVE STRENGTH

LIME HYDRATE STUDY

A study was conducted using five different lime hydrates to determine their suitability for carbonate bonding. Table 2 lists the manufacturers

and typical analyses for each of the lime hydrates. Since the five lime hydrate samples had different calcium oxides contents and different external surface areas, the Ohio Super Spray was used as a standard. In prior experiments, 20 weight percent of Ohio Super Spray was used; consequently, the other five lime hydrate samples were adjusted to yield approximately the same weight ratio of calcium oxide to taconite tailings as used with Ohio Super Spray. The calcium oxide to taconite tailings weight ratio varied between 0.11 and 0.12 for the various lime hydrates.

Briquettes were prepared using 3 percent water and an initial formation load of 84 kg/cm^2 (1200 psi). The briquettes were then reacted for six hours using 100 percent dry carbon dioxide and allowed to cure for 190 hours prior to determining the compressive strength. The compressive strengths for the various lime hydrate-taconite tailings briquettes were then adjusted to a steady state value using Figure 6. The compressive strengths at 190 hours and at steady state (700 hours) of the various lime hydrates briquettes are listed in Table 3. The results of Table 3 indicate that Pfizer's spray lime hydrate yielded the highest compressive strength (337 kg/cm^2 [4800 psi]) and that Ohio Super Spray and National Hydrate were next best at 278 and 260 kg/cm^2 (4000 and 3700 psi), respectively.

Table 3
Compressive Strength of the Lime Hydrate Briquettes*

	Compressive Strength, kg/cm^2	
Lime Hydrate	190 hours	700 hours
Ohio Super Spray	239	278
Pfizer Spray	295	337
Tiger Finish	140	162
National Hydrate	225	260
Marble Cliff	77	88
Mercer Lime	22	26

*Using dry CO_2

In the actual operation of the carbonate bonding process, a water bearing flue gas containing carbon dioxide will be used to carbonate bond the lime hydrate taconite mixture. Therefore, an experiment was conducted using briquettes made from the six lime hydrate samples and water saturated 100 percent carbon dioxide. The briquettes were placed in the reaction chamber and carbon dioxide gas bubbled through a column of water. After a reaction time of six hours, the briquettes were removed and allowed to cure for 190 hours. The compressive strength was then determined for the briquettes. The results of these experiments are shown in Table 4.

Table 4
Compressive Strength of the Lime Hydrate Briquettes*

Lime Hydrate	Compressive Strength, kg/cm^2	
	190 hours	700 hours
Ohio Super Spray	276	315
Pfizer Spray	176	201
Tiger Finish	148	169
National Hydrate	223	255
Marble Cliff	84	96
Mercer Lime	35	40

*Using water saturated CO_2

In comparing Table 3 (dry CO_2) with Table 4 (wet CO_2), it is seen that the compressive strength of each lime hydrate increased using a water saturated carbon dioxide except for the Pfizer Spray which decreased from 337 to 201 kg/cm^2 at steady state. Also, by using a water saturated carbon dioxide gas, the Ohio Super Spray briquettes increased from 278 to 315 kg/cm^2. Thus, under the more representative carbonate bonding condition of water saturated carbon dioxide, Ohio Super Spray* is the most suitable lime hydrate. In a commercial application of the carbonate bonding process, carbon dioxide will be formed by burning a fuel and water vapor will be present in the gas.

There are other factors besides the calcium oxide content of lime hydrate which can affect the extent of the carbonate bonding reaction and the resulting briquette compressive strength. The external surface area of the lime hydrate plays an important role because as the surface area increases, more carbonate bonding reaction area is available to yield a denser and stronger limestone matrix. Thus, external surface area which is a function of particle size and the lime hydrate manufacturing procedure is indicative of the resulting carbonate bonding strength. This is shown in Figure 10 where the steady state compressive strength of each lime hydrate from Table 3 (dry carbon dioxide) is plotted versus the external surface area of the lime hydrate per gram of taconite tailings. In Figure 10, compressive strength increases substantially with increasing external surface area. Other lime hydrate factors influence compressive strength. One such factor which probably affects strength is the lime hydrate's MgO content. As seen in Tables 2 and 3, the more successful lime hydrates tended to have higher MgO contents. For example, Marble Cliff lime hydrate which has an external surface area comparable to National Lime Hydrate (5698 cm^2/gram compared to 6404 cm^2/gram) yielded a considerably lower compressive strength probably because of its lower MgO content (5 percent as compared to 34 percent for National Lime Hydrate).

*Mention of trade names in the report does not imply endorsement or recommendation by either Applied Technology Corporation or the Environmental Protection Agency.

While determination of the exact reasons why one lime hydrate is more suitable than another is beyond the scope of study, it can be stated that dolomitic lime hydrates with high external surface areas yield the highest compressive strengths.

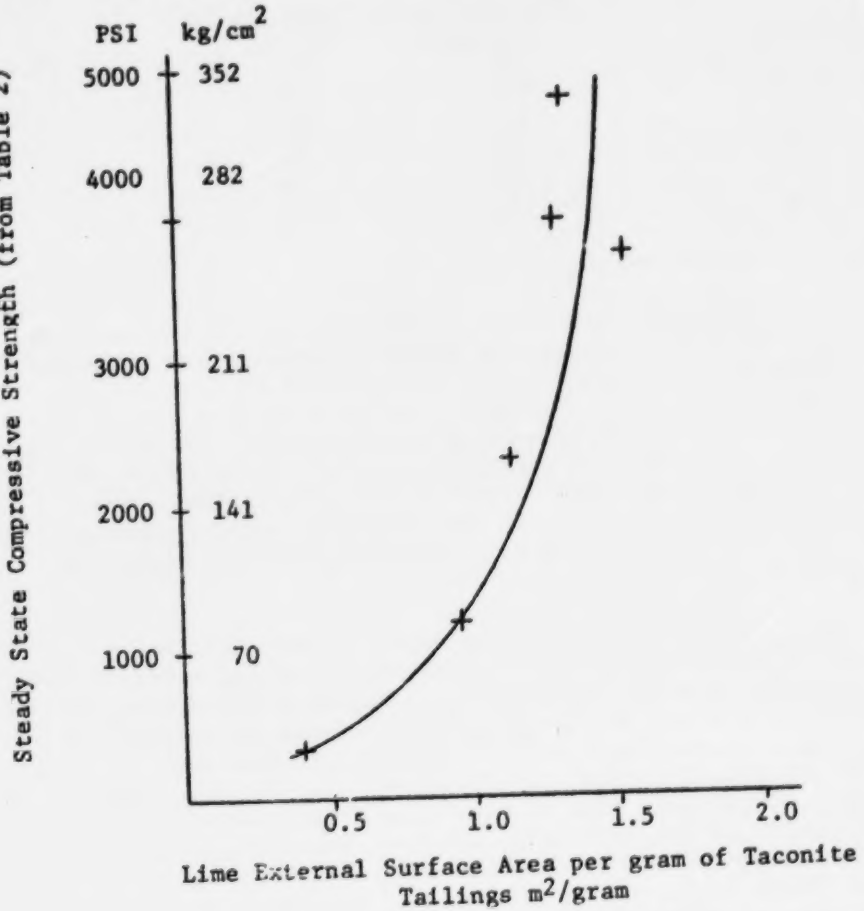


FIGURE 10--EFFECT OF LIME EXTERNAL SURFACE ARE ON COMPRESSIVE STRENGTH (DRY CARBON DIOXIDE)

Based on the lime hydrate study, Ohio Super Spray and two addditional lime hydrates, Pfizer Spray and National Hydrate, were selected for further study.

In addition to compressive strength, the resulting carbonate bonded briquettes must possess other requisite properties to produce suitable construction materials. The carbonate bonded product must be able to prevent or minimize the permeation of water and air and possess a resistance

to weathering. If carbonate bonded taconite tailings cannot maintain structural integrity during repeated freezing and thawing, then it cannot be an effective construction material. The properties that were investigated and will be presented in the next section are air and water permeability of taconite tailings, the compressive strength after repeated freeze-thaw cycles, and flexural strength.

AIR AND WATER PERMEABILITY OF CARBONATE BONDED TACONITE TAILINGS

A search of the ASTM standards did not yield an applicable standard determination for air and water permeability, therefore, special equipment and procedures were established for these determinations based on the commonly accepted theory of permeability. The equipment and procedures are discussed in the Appendix. Where applicable, cement briquettes were used as a basis for comparison. These cement briquettes were prepared using one part (by weight) Portland Type One cement, 2.75 parts Ottawa Sand and 1/2 part water. The cement and sand were dry mixed, the water added slowly, and the wet mixture blended thoroughly. The cement briquettes were allowed to cure 28 days.

The experimental procedure to determine air permeability consisted of using a taconite tailings briquette as a plug in a sealed chamber. The chamber pressure was then determined as a function of time. This is an unsteady state operation in which the pressure driving force is continually changing with time. The mathematical treatment required to obtain the air permeability is presented in the Appendix. The air permeability is defined as the volumetric flow rate of air (m^3/hr) per cross-sectional flow area (m^2) per unit pressure driving force ($kg/m2/m$).

In this test the air permeability of Ohio Super Spray lime hydrate, Pfizer Spray lime hydrate, and National Lime Hydrate taconite tailings briquettes were determined. For comparative purposes, the air permeability of a cement briquette of the same dimensions as the taconite tailings briquettes was also determined. The results are presented in Table 5 where the air permeability, and the ratio of the permeability of the taconite tailings briquettes to the cement briquette are presented.

Table 5
Air Permeability of Taconite Tailings Briquettes

Lime Hydrate	Air Permeability*	Permeability Ratio**
Ohio Super Spray	1.01×10^{-6}	1.6
Pfizer Spray	1.01×10^{-6}	1.6
National Hydrate	0.63×10^{-6}	1.0
Cement	0.63×10^{-6}	-

*$m^3/(hr-m^2-[kg-m^2/m])$

**$\frac{\text{Air Permeability of Lime-Hydrate Taconite Briquettes}}{\text{Air Permeability of Cement}}$

The water permeability of taconite tailings briquettes was determined in much the same manner as air permeability and is discussed in the Appendix. Water permeability is the mass flow rate of water per cross-sectional flow area per unit pressure driving force. The water permeability of Ohio Super Spray, Pfizer Spray, and national Hydrate taconite tailings briquettes is shown in Table 6. Also shown in Table 6 is the water permeability ratio defined as the water permeability of taconite tailings divided by the water permeability of cement. It is interesting to note the varitions in water permeability of the lime hydrate taconite tailings briquettes. The Ohio Super Spray compares quite well with cement in the prevention of water permeation. The Pfizer Spray and the National Lime taconite tailings briquettes proved to be inferior in the prevention of water permeation and would probably not provide an adequate seal against water permeation. On the other hand, the Ohio Super Spray-taconite briquette would provide an adequate seal against water permeation.

Table 6
Water Permeability of Taconite Tailings Briquettes

Lime Hydrate	Permeability*	Permeability Ratio**
Ohio Super Spray	9.8×10^{-10}	2.3
Pfizer Spray	6.7×10^{-8}	160.0
National Hydrate	9.4×10^{-9}	22.0
Cement	3.9×10^{-10}	--

*Water Permeability in $kg/(hr\text{-}m^2\text{-}[kg/m^2/m])$
**Permeability of lime taconite/permeability of cement

The air and water permeability results obtained are somewhat inconsistent. The order of permeability for the various lime hydrates should be the same for air and water permeation, as both permeabilities are a function of porosity. As a possible explanation for the varying permeabilities of the lime hydrates, it is postulated that water is reacting with the lime hydrate to change its porosity whereas air would not be expected to react. This would account for the significant differences in water permeability shown in Table 6 for the various lime hydrates. Nevertheless, the permeability results are still applicable.

FREEZE-THAW TEST ON CARBONATE BONDED TACONITE TAILINGS

Freeze-thaw tests were performed on briquettes formed using Ohio Super Spray, Pfizer Spray and National Hydrate. The freeze-thaw test was based on the ASTM designation: C290-67 entitled "Standard Method of Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water." The freeze-thaw test, as modified for this study, is discussed in the Appendix. The objective of this test was to determine compressive strength of the lime-hydrate taconite tailings briquettes as a function of the number of freeze-thaw cycles for the three lime hydrates briquettes. As seen in Figure 11, the compressive strength of the briquettes tend to

stabilize at a relatively constant value after five freeze-thaw cycles. After 40 cycles, briquette compressive strength varied between 169 kg/cm^2 (2400 psi) for National Hydrate to 211 kg/cm^2 (3000 psi) for Ohio Super Spray.

It must be noted that subjecting a composite material of small dimensions (five cm diameter by five cm high briquettes) to 40 freeze-thaw cycles is an extreme test. The ASTM standard test method contemplates the use of specimens not less than 7.6 cm nor more than 12.7 cm in width and depth and not less than 35.6 cm nor more than 40.1 cm in length. The normal erosion of surface edges which occurs during freeze-thaw testing does not seriously affect large specimens, whereas for small briquettes the effect on strength is quite dramatic as evidenced by the results of this study.

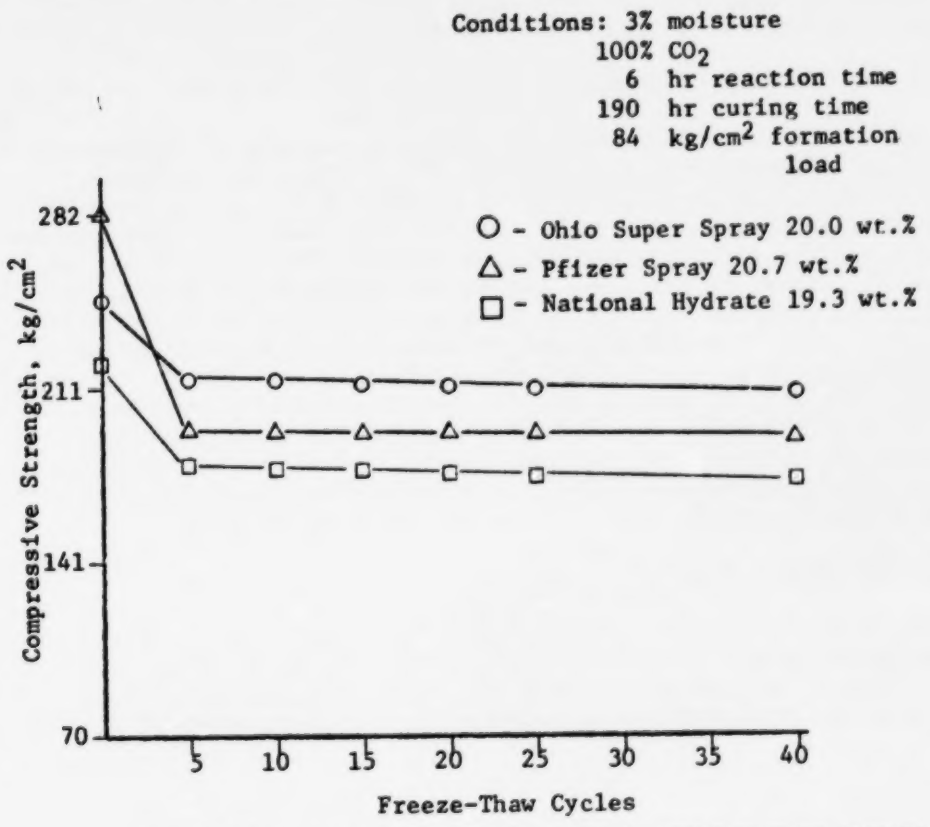


FIGURE 11--COMPRESSIVE STRENGTH VS. FREEZE-THAW CYCLES

An examination of the lime hydrate taconite tailings briquettes after 40 cycles revealed an erosion of about 0.6 cm of material almost completely around the edges of the Pfizer lime and National Hydrate. The edges on the Ohio Super Spray lime hydrate taconite tailings briquetts revealed less than

0.3 cm material loss. This reduced area on which the compressive strength test load was applied caused the briquettes to fail at lower loads and indicates a lower compressive strength than those based on the original 20.3 cm^2 area. For comparison, cement briquettes had an initial compressive strength of 140 kg/cm^2 which reduced to 84 kg/cm^2 after 40 freeze-thaw cycles. An examination of the cement briquettes after 40 cycles revealed an erosion of about 0.3 cm of material almost completely around all edges.

Even under extremely unfavorable test conditions, the carbonate bonded taconite tailings briquettes yielded compressive strengths in the order of 169 to 211 kg/cm^2. Consequently, it should withstand the effects of severe changes in temperature. Ohio Super Spray lime hydrate yielded the highest compressive strength (211 kg/cm^2) after 40 freeze-thaw cycles.

FLEXURAL STRENGTH TESTS ON CARBONATE BONDED TACONITE TAILINGS

A study was conducted to determine the flexural strength of the three superior lime hydrates, Ohio Super Spray, Pfizer Spray and National Hydrate. In the flexure test, a load is applied at the center of a bar that is supported near its two ends. As the load increases, the specimen bar exceeds its elastic limit and failure occurs. The load applied at failure is calculated in kilograms per square centimeter. Several bars measuring 2.54 cm square by 10.16 cm long were prepared using the three lime hydrates. The flexural strength of taconite tailing bars using Ohio Super Spray, Pfizer Spray and National Hydrate were 35, 31 and 24 kg/cm^2 (500, 440 and 340 psi), respectively. The flexural strength of concrete is normally about one-tenth its compressive strength. The highest flexural strength for the lime taconite tailings bars was about one-eighth their compressive strength. Both the Ohio Super Spray and Pfizer Spray limes exceeded the flexural strength of concrete.

SUBSEQUENT EXPERIMENTATION

As a result of the briquette laboratory study, it was decided to select Ohio Super Spray as the lime hydrate to use in subsequent brick and plot testings. Except for the air permeability test, the Ohio Super Spray taconite tailings briquettes were superior to the other selected lime hydrates.

SECTION V

EXPERIMENTAL STUDY (BRICKS)

CARBONATE BONDING OF TACONITE TAILINGS AS 15 cm CUBES

In the Appendix entitled "Theoretical Considerations of Carbonate Bonding" a simplified model of carbonate bonding is presented. This model considers that the progression of an interface separating a carbonate bonded zone from an unreacted zone in a slab of lime hydrate bearing material is controlled by the diffusion of carbon dioxide into the slab. The model predicts that the progress of the carbonate bonded interface is related to the square root of time:

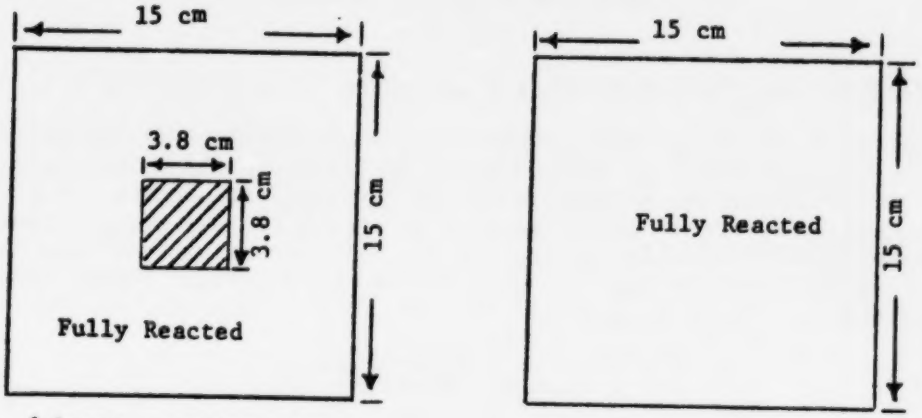
$$z' = \sqrt{4kt} \qquad (1)$$

where z' = the depth of the carbonate bonded layer into the slag at any time
k = constant
t = time

Furthermore, the model predicts that the rate of diffusion of CO_2 is directly proportional to the concentration of the CO_2 in the reaction gas and for a given reaction time the depth of the carbonate bonded zone will be directly proportional to the CO_2 concentration in the reaction gas. The model was primarily developed to ascertain the required carbonate bonding time for plot experimentation. Plot experimentation involved the carbonate bonding of plots, 1.2 metres square, and will be discussed in a later section.

To check the model and ascertain the required carbonate bonding time for plot experimentation, 15 cm taconite cubes were carbonate bonded at various CO_2 concentrations and carbonate bonding times, using Ohio Super Spray lime hydrate. These experiments were conducted by placing the pressed cube in a sealed container which had inlet and outlet valves. CO_2 was introduced and the reaction took place over the entire surface of the brick. After the allotted time, the bricks were cut in half and the extent of carbonate bonding measured.

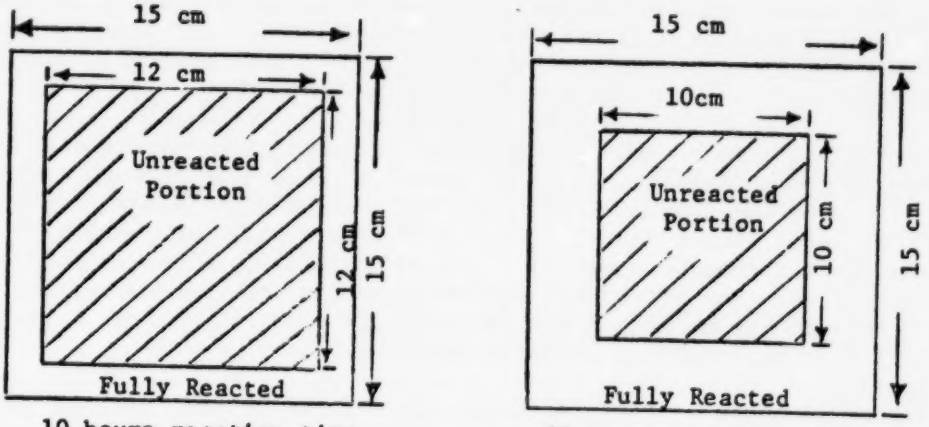
Figure 12 shows a cross-sectional view of two bricks, reacted with 100 percent CO_2 for times of six and ten hours. After a total reaction time of six hours, the carbonate bonded interface progressed to a depth of 5.7 cm. After ten hours reaction time, the entire brick was reacted (7.6 cm progression). Another series of experiments were conducted to simulate carbonate bonding with flue gas. A gas mixture containing 20 percent CO_2 and 80 percent N_2 was used for ten and twenty hour periods. These bricks are shown in Figure 13 where it is seen that the carbonate bonded interface progressed a distance of 1.6 cm and 2.4 cm for reaction times of ten and twenty hours, respectively.



6 hours reaction time
shaded portion -- unreacted

10 hours reaction time

FIGURE 12--SECTIONED BRICKS REACTED WITH 100% CO_2



10 hours reaction time

20 hours reaction time

FIGURE 13--SECTIONED BRICKS REACTED WITH 20% CO_2

The results of the above experiments were plotted in Figure 14 as the carbonate bonded depth versus the square root of the carbonate bonding time. For both the 20 and 100 percent CO_2 cases, the curves are straight which infers that equation (1) is a valid representation of the progression of the carbonate bonded interface. That is, the progression of the carbonate bonded layer is directly proportional to the square root of carbonate bonding time as predicted by the model.

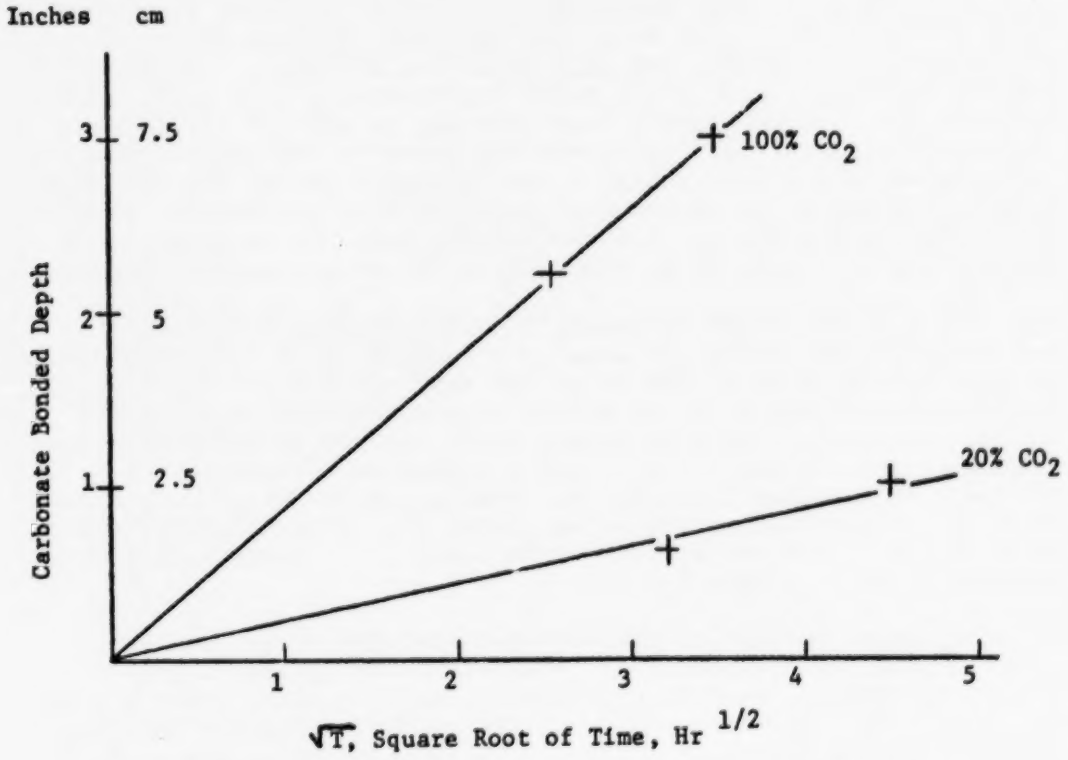


FIGURE 14--CARBONATE BONDED DEPTH VS TIME FOR 15 cm BRICK

The slope of the lines shown in Figure 14 are 2.1 and 0.55 cm/(hr)$^{1/2}$ for the 100 and 20 percent CO_2 cases. The ratio of these slopes is 4.8 which is very close to mass-transfer driving force ratio:

$$\frac{(C_R-C_I)\ 100\%\ CO_2}{(C_R-C_I)\ \ 20\%\ CO_2} = \frac{100-0^*}{20-0} = 5$$

where C_R = concentration of CO_2 in the reaction gas
C_I = concentration of CO_2 at the carbonate bonding interface
$^*C_I$ is assumed to be zero

Thus, as indicated by the model, the carbonate bonding depth at any given time is directly proportional to the CO_2 concentration in the gas provided similar formation loads are used. Figure 14 can be used to estimate the required carbonate bonding time for a lime hydrate bearing slab of specified thickness.

A study was undertaken to evaluate the effect of formation load on the depth of carbonate bonding using the 15 cm cubes. Cubes were prepared using 20 percent Ohio Super Spray lime hydrate, 3 percent moisture, 100 percent carbon dioxide gas, and reacted for six hours. Formation loads in the range of 35 to 105 kg/cm^2 (500-1500 psi) were used. After reaction, the carbonate bonded cubes were cut in half and the depth of the carbonate bonded layer measured. The objective was to determine if there was any significant change in the carbonate bonding rate due to porosity changes in the taconite tailing-lime hydrate structure which would affect the diffusion of carbon dioxide gas. The formation loads selected are considered to be those obtainable using commercial equipment.

The results of this study are shown in Figure 15 where the depth of the carbonate bonded layer is shown as a function of the formation load. Cubes formed at 35 kg/cm^2 had an average depth of reaction of 4 cm whereas cubes formed at 105 kg/cm^2 had an average reaction depth of 3.8 cm. Considering the experimental error involved in these measurements, it appears that formation load is not a significant factor--at least for the range of formation load studied. However, while formation load may not have a significant effect on the progression of a carbonate bonding layer, it has a very definite effect on compressive strength (see Briquette Study -- Figure 9).

The compressive strength of the sectioned cube (Figure 12, ten hour reaction time, fully carbonated) was determined to be 226 kg/cm^2 (3200 psi) using a formation load of 54 kg/cm^2 (770 psi). This is significant in that taconite tailings bricks could be formed at formation loads higher than 84 kg/cm^2 (1200 psi) to yield bricks as strong or stronger than concrete. This would be another outlet for the use of taconite tailings.

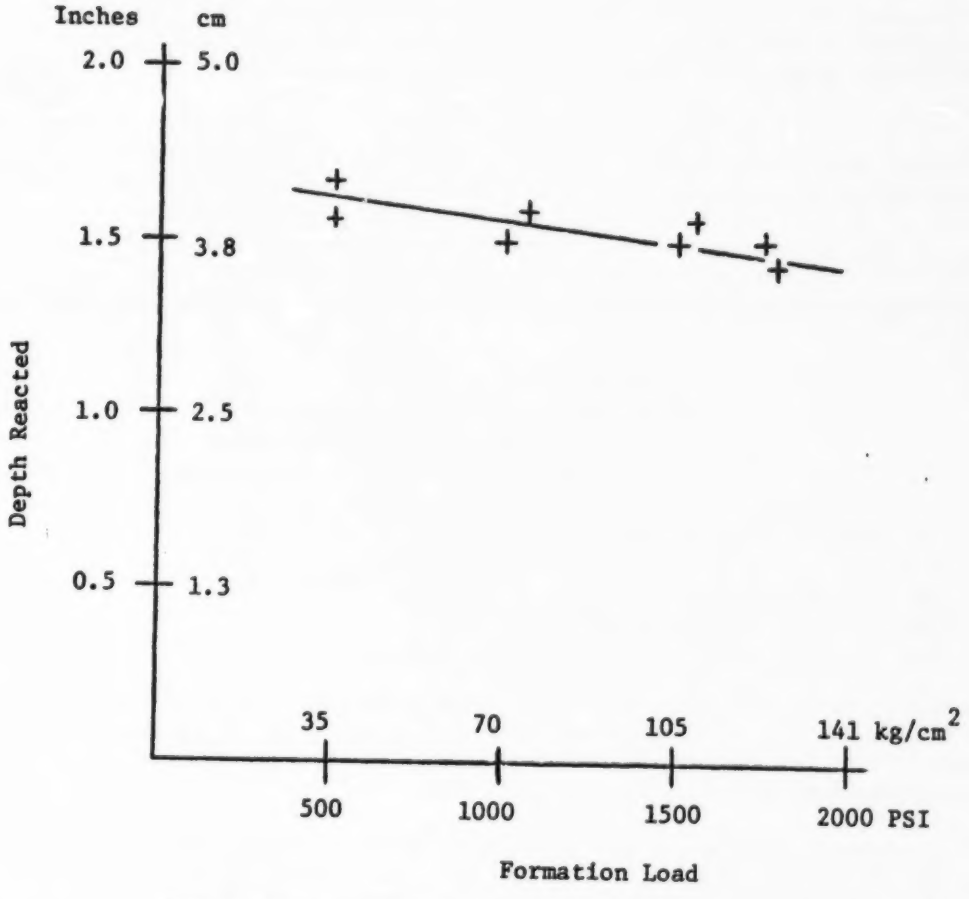


FIGURE 15 - EFFECT OF FORMATION LOAD ON DEPTH OF CARBONATE BONDING OF 15 cm BRICKS

SECTION VI

TACONITE TEST PLOTS

Based on the results of the bench-scale tests, Ohio Super Spray lime hydrate at 20 weight percent, a 3 percent moisture content, and a 100 percent carbon dioxide reaction gas were selected for the plot study. Using these conditions, several test plots were prepared. The purpose of the plots was to investigate various carbon dioxide addition techniques under conditions more nearly approaching road building techniques.

Five 1.2 metre square plots were prepared. Figures 16 and 17 show the configuration of these plots. Each was formed such that the top surface was at ground level with 10.1 cm of compacted lime hydrate-taconite mixture carbonate bonded. Various carbon dioxide addition techniques were explored. A summary of the base material and lime hydrate taconite mixture thickness is presented in Table 7 for the five plots.

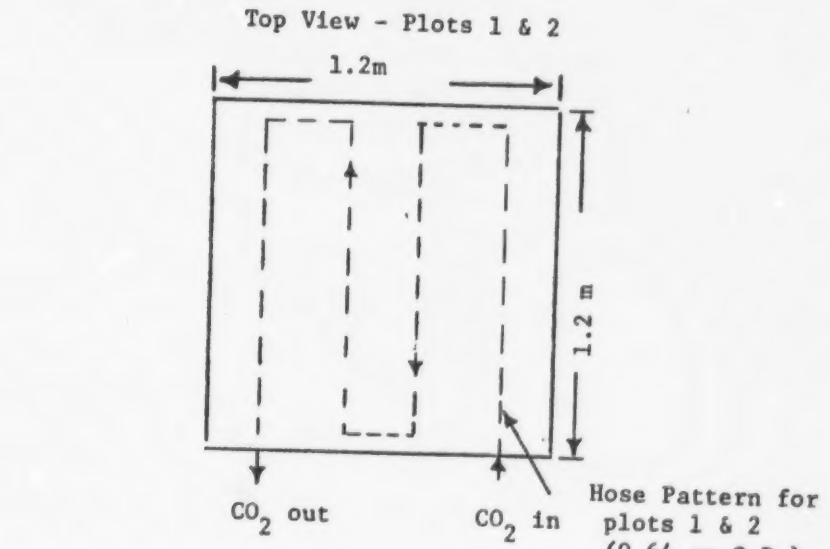
Table 7
Plot Thickness

Plot	Base	Compacted Lime Hydrate-Taconite Thickness, cm	Plot Thickness, cm
1	Fine gravel (5.1 cm layer)	10.1	15.2
2	None	10.1	10.1
3	Fine gravel (5.1 cm layer)	10.1	15.2
4	Coarse gravel (5.1 cm layer)	10.1	15.2
5	Sand (5.1 cm layer)	10.1	15.2

Plot 1 had a 0.64 cm diameter perforated hose positioned in a pattern as shown in Figure 16. On top of the hose a 5.1 cm layer of gravel was spread. The lime hydrate-taconite mixture was then spread over the gravel and compacted to a thickness of 10.1 cm.

Plot 2 also shown in Figure 16 was similar to Plot 1 except that no gravel was used and the total plot thickness was 10.1 cm. Plots 3, 4, and 5 used different base materials as shown in Table 7. These plot configurations are shown in Figure 17 where it is seen that carbon dioxide was admitted at the center for all three plots.

To prepare the plots, the lime hydrate-taconite mixture was spread over the base material (gravel or sand with carbon dioxide carrier gas hose embedded) and compacted with a small (low load generating) motorized roller. The compacted mixture was then carbonate bonded using cylinders of carbon dioxide gas according to the flow rate schedule shown in Table 8. An excess (assuming no leaks) of CO_2 (16-24 hr period) was added to insure full carbonate bonding. Table 8 was prepared using the theoretical carbonate bonding model developed in this work in which the depth of carbonate



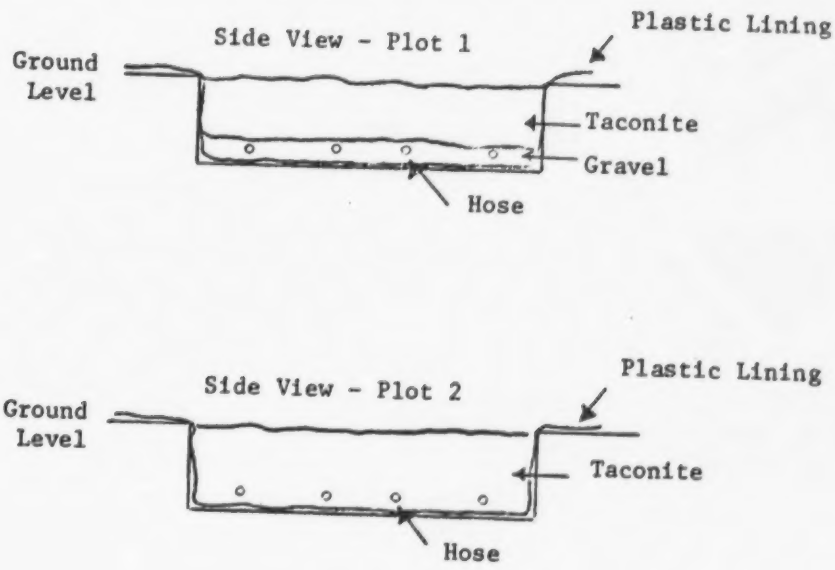


FIGURE 16--CONFIGURATION OF PLOTS 1 & 2

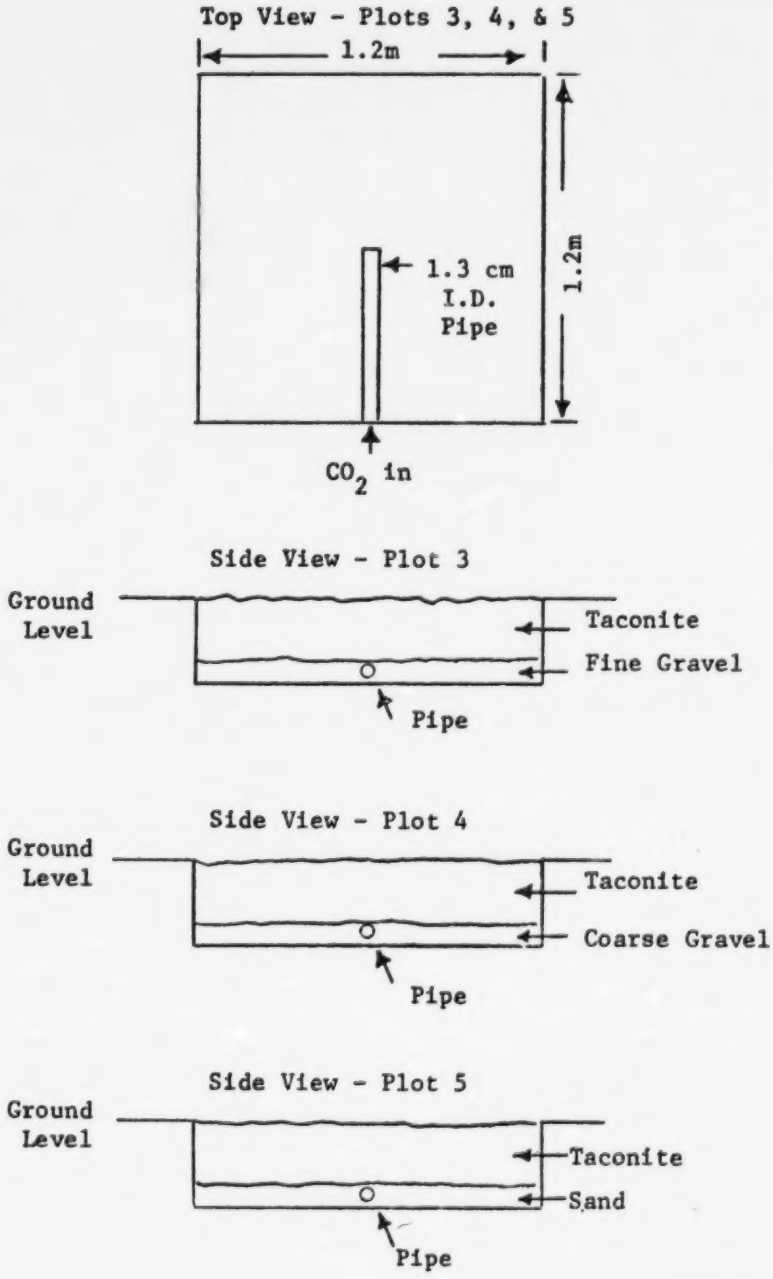


FIGURE 17--CONFIGURATION OF PLOTS 3, 4, & 5

bonding as a function of time was determined. The data generated in the brick study was used to evaluate the various constants in the resulting expressions.

Table 8
Plot CO_2 Addition Rate

Time Period	CO_2 Flow Rate (liter/hour)
0-1/2 hr	4950
1/2-2	1700
2-4	850
4-16	340
16-24	142

Unfortunately, prior to preparing these outdoor plots, it had rained intermittently for several weeks and the ground became saturated with water. During compaction, the roller had to be driven over the saturated ground and onto the lime hydrate-taconite mixture. While the roller was compacting the plots, the surrounding ground was giving way and insufficient compaction of the plots resulted. In addition, because of the area limitations of the plots (1.4 metres square) a sufficiently large roller could not be used to generate formation loads in the order of 70 kg/cm^2 (1000 psi). The weight of the motorized roller was approximately 1360 kgs (3000 lb). Each of the two rollers of the motorized roller was 0.61 meter (2 ft) long. Assuming a contact area of 0.64 cm (0.25 inches) for each roller, the resulting formation load was estimated to be 35 kg/cm^2 (500 psi). Thus, in essence, ATC could not apply the desired formation load (70 kg/cm^2 [1000 psi]) to form these plots. After all five plots were compacted and reacted, they were allowed to cure to permit the strength of the lime-taconite mixture to reach steady state. The plots were then sampled at several locations and tested for percent carbonation, compressive strength, and density.

The percent carbonation was defined as:

$$\text{Percent Carbonation} = \left(1 - \frac{W_F}{W_I}\right) 100$$

where W_I = initial weight fraction of lime hydrate in the mixture

W_F = final weight fraction of unreacted lime hydrate in the carbonate bonded material

Percent carbonation was determined by reacting a sample of the carbonate bonded taconite with hydrochloric acid and measuring the amount of carbon dioxide evolved. From the known amount of lime hydrate used and the amount of carbon dioxide evolved following reaction, the percent carbonation was determined.

Figure 18 shows the location of the sampling sites. Samples from locations A1 to A3 were tested for percent carbonation and compressive strength whereas apparent densities were determined from the samples at locations B1 to B3.

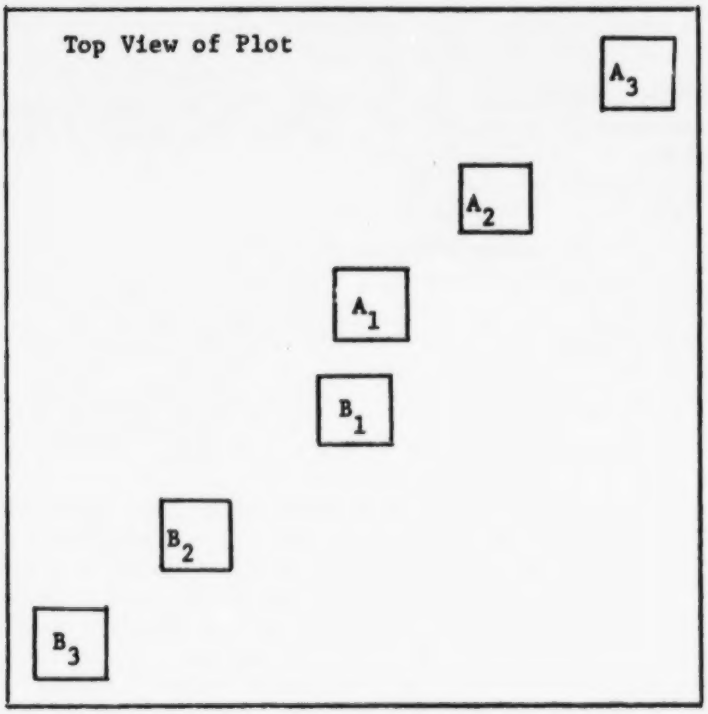


FIGURE 18--LOCATION OF SAMPLING SITES IN EACH TEST PLOT

Attempts were made to take samples from Plots 1 and 2 but the plots had not bonded well (probably due to rainfall and insufficient compaction) and core samples could not be taken. Samples were obtained from Plots 3, 4, and 5. In Table 9 is shown the compressive strength and density for the various samples of Plots 3 to 5. Examination of the results in Table 9 and the sampling locations of Figure 18 indicate that the compressive strength increases as the sampling location approached the center of the plot (where the single carbon dioxide source was located). At first, it appeared reasonable to say that most of carbonate bonding occurred at the CO_2 source (center of the plot). Upon closer examination, however, the percent carbonation (extent of carbonate bonding) was not significantly different (18 to 20 percent) at the various sampling sites. In all probability, the center of the plot was formed with a higher formation load which yielded higher compressive strength. This is somewhat substantiated by the increase in density observed as the center of the plot is approached. Thus, the strength of the carbonate bonded plot is strongly dependent on the formation load.

Since the percent carbonation did not vary significantly across the plot, it can be said that the single source of CO_2 whether located in fine gravel, coarse gravel, or sand did not significantly affect the distribution of CO_2. The fact that this relatively even distribution of CO_2 results (even with a single source of CO_2 in a 1.2 metre square)

Table 9

Test Results for Plots 3, 4, & 5

Plot	Location[1]	Percent Carbonation	Compressive Strength Kg/cm^2 (psi)	Location[2]	Density, g/cc
3	A1	20	105	B1	2.73
	A2	20	84	B2	2.49
	A3	20	0	B3	2.21
4	A1	20	84	B1	2.51
	A2	19	70	B2	2.20
	A3	20	0	B3	2.09
5	A1	20	70	B1	2.25
	A2	18	70	B2	2.13
	A3	18	0	B3	2.02

1 Tested for percent carbonation and compressive strength

2 Tested for density

is significant in that it demonstrates the feasibility of road building using perforated tubing at 1.2 metre (4 foot) centers (road building applications will be discussed in a subsequent section).

In Figure 19 the compressive strengths of sample "A" are plotted versus the density of corresponding "B" samples (data from Table 9). There is a relationship between density and compressive strength; the compressive strength increases as the density increases. Since the percent carbonation is approximately the same, it can again be deduced that the formation load must have varied at the different locations.

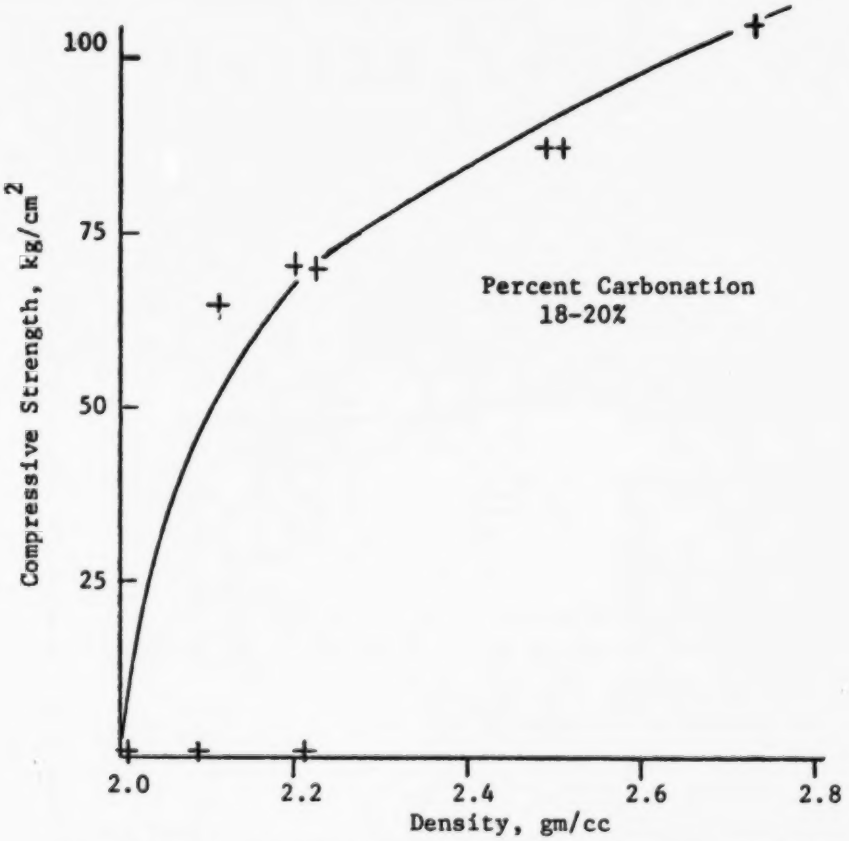


FIGURE 19--COMPRESSIVE STRENGTH VS DENSITY FOR PLOTS 3,4,& 5

The compressive strength of samples taken near the center of the plot where it may be assumed that the roller formation load was 35 kg/cm^2 (500 psi) agrees with the briquette formation load affect illustrated as Figure 9. Figure 9 predicts a compressive strength of about 84 kg/cm^2 (1200 psi) and plot compressive strengths between 70 and 105 kg/cm^2

(1000 and 1500 psi) were achieved. It might be deduced that if higher formation loads were possible for plot preparation, compressive strength comparable to those obtained in the briquette study would have been achieved.

In summary, the plot results are encouraging in that they correlate well with the briquette study. Unfortunately, due to plot/roller size limitation and inclement weather, the desired and commercially obtainable formation load could not be realized. Considerably more work will be required to develop carbonate bonding road building techniques under actual field conditions.

SECTION VII

APPLICATION OF CARBONATE BONDED TACONITE TAILINGS

The primary objective of this study was to determine the feasibility of utilizing taconite tailings as a fill material in the carbonate bonding process. The results of this study show that carbonate bonded taconite tailings have the necessary strength properties for paving applications and the necessary sealant properties to effectively prevent permeation of water which causes degradation of paved roads. The carbonate bonded process utilizing taconite tailings could be employed to (1) construct secondary roads utilizing the formed carbonate taconite tailings as is, (2) provide a strong inexpensive base material for major road construction, (3) provide a first class road when used in conjunction with a thin layer of asphalt, (4) provide aggregate as a base material, and (5) make bricks. These applications have the advantage that taconite tailings can be used up, thereby, reducing stockpiles and minimizing their polluting effect.

PROCESS DESCRIPTION

Although no work has been completed on larger scale field testing of the carbonate bonding process employing taconite tailings, the following proposed commercial concept appears feasible for the construction of roads. It is to be noted that suitable techniques will have to be developed to permit carbonate bonding under inclement weather conditions. The dried taconite tailings material is mixed with lime hydrate and water (if necessary) in the proper proportions to make a homogeneous mixture of lime hydrate and taconite tailings. A perforated plastic pipe is placed at 1.2 metre centers on the base of the road bed. Gravel or sand can be placed over the road bed and over the perforated hose. The lime hydrate taconite mixture is then spread over the hose which is expendable and a roller is driven over the mixture to compact it. After compaction the perforated hose is attached to a portable carbon dioxide generator which can be a burner of coal, oil, or any other carbonaceous fuel which generates products of combustion containing carbon dioxide.

The flue gases are pumped under pressure into the perforated plastic hose. The conversion of lime hydrate to carbonate once completed forms a road bed that will be surface hardened with a concrete like covering. At present, the effect of combustion products other than carbon dioxide and water vapor on the carbonate bonding reaction is not known. Since these gases will consist mainly of nitrogen, unburnt oxygen, and hydrocarbons, it is anticipated that there will be little or no effect. In this study, experiments conducted with water saturated carbon dioxide indicate that wet gas increased the lime hydrate taconite compressive strength.

As is evident from the foregoing description, the process can use existing road grading equipment, requires no unusually skilled labor, and can use locally available materials (with the exception of the lime hydrate) thus minimizing material handling. To carry out the process, the following items of equipment will be required:

1. Expendable perforated plastic hose
2. Earth moving and compacting equipment
3. A portable carbon dioxide generator
4. Large capacity mixers (cement mixing truck)

The earth moving, compacting, and mixing equipment are not unique and are considered part of the normal inventory of maintenance construction equipment. The portable carbon dioxide generator can also be readily fabricated. The equipment would essentially consist of a burner and a blower. The burner which can operate on a convenient fuel (coal, fuel oil, bottled gas, or other carbonaceous fuels) would generate products of combustion containing 15 to 20 percent carbon dioxide. These flue gases would be compressed and introduced into the perforated hose. If rapid setting of the carbonate bonded material is required, concentrated carbon dioxide can be generated by the addition of an amine absorber to the above equipment. Economics will dictate the type of carbon dioxide generator.

SUGGESTED OPERATING PARAMETERS

The economics of carbonate bonded taconite tailings depend primarily on four controllable factors: moisture content of the taconite tailings, quantity of lime hydrate required, carbon dioxide concentration, and the carbonation time.

The moisture content of the taconite tailings has been shown to be an important factor. To obtain maximum compressive strength, the moisture content of the taconite tailings must be in the range of 3 to 5 percent.

This study has shown that a maximum of 20 percent lime hydrate will yield compressive strengths approaching 316 kg/cm^2 (4500 psi) for taconite tailings. Should lower compressive strength be acceptable, the amount of lime hydrate can be decreased accordingly.

It has been found that adequate carbonate bonded taconite tailings strengths are achieved when a 20 percent carbon dioxide gas mixture is used for reaction times of ten hours. Assuming that faster set times are not required, a simple inexpensive carbon dioxide gas generator can be used to yield carbon dioxide concentrations of about 15 to 20 percent. Faster set times will require the use of carbon dioxide generators producing a higher purity gas.

PROCESS ECONOMICS

Costs for using carbonate bonding as a method of road construction can only be approximated as full scale paving tests have not been performed. These costs can be generated by considering the paving costs for conventional materials shown in Table 10.

Table 10
Paving Cost, $/sq. yard

Construction Material	Material in Place*	Labor**	Materials**
4-inch rigid concrete	11.5	7.3	4.2
6-inch rigid concrete	11.3	7.2	4.1
8-inch rigid concrete	13.9	8.8	5.04
4-inch sub-base	2.0	-	-
6-inch sub-base	2.4	-	-
8-inch sub-base	2.1	-	-
6-inch Bituminous pavement w/base course	4.0	0.7	3.3
9-inch Bituminous pavement w/base course	11.5	2.1	9.4
12.5-inch Bituminous pavement w/base course	13.0	2.4	10.6

*Pennsylvania Department of Transportation, Bulletin 50-Construction Cost Catalog (Sept., 1973).
**Labor/material = 1.75 (concrete paving), 0.22 (asphalt paving), Popper, H., "Modern Cost Estimating Techniques," McGraw-Hill Co., New York, p. 101 (1970)

As this information has been obtained from the above indicated source, it is presented in the units of the source. For comparative purposes, carbonate bonding costs are presented in the same units.

As stated previously, labor costs using carbonate bonding are not available. Although the techniques and equipment required for paving with the carbonate bonding process will probably not differ significantly from asphalt paving, the labor cost associated with drying, mixing, and carbon dioxide generation will be greater than those of asphalt paving. Therefore, for a conservative cost comparison, the carbonate bonding labor cost has been assumed to be the same as for concrete (Table 10). Paving costs for carbonate bonding were then developed on this basis and are shown in Table 11. For the material costs of Table 11, it was assumed that taconite tailings are available at no cost, with the cost of transportation, drying, mixing, etc., included in the labor cost. Lime hydrate was assumed to be $25 per ton (bulk) delivered, and 20 percent lime hydrate was used in the fill material. In Table 11, the lime hydrate cost, the cost of perforated hose, and cost of fuel required to generate carbon dioxide are presented as a function of thickness. The cost of fuel is directly proportional to the carbonate bonding thickness. To

determine the cost of perforated hose, it was assumed that the hose would be located on four foot centers in the pavement, and for thicknesses greater than six inches, two layers of hose would be required.

Table 12 was prepared to illustrate road construction costs of conventional paving materials, carbonate bonded taconite tailings, and combinations of both using the paving costs of Tables 10 and 11.

Table 11
Paving Cost for Carbonate Bonding, $/sq. yard

Thickness	Total Cost	Labor Cost*	Material Cost		
			Lime Hydrate	Hose**	Fuel
4 inch	8.6	7.3	0.92	0.12	0.24
6 inch	9.0	7.2	1.38	0.12	0.34
8 inch	11.3	8.8	1.85	0.24	0.40

*Labor cost for concrete, Table 10
**Hose cost is $0.04 per linear foot

For secondary road construction, Table 12, the application of carbonate bonded taconite tailings offer no significant cost advantage or disadvantage over conventional materials. That is, despite the much higher assumed labor costs for carbonate bonding, total paving costs for secondary roads are comparable to conventional paving materials.

For first class roads, Table 12, carbonate bonded taconite tailings offer a definite cost advantage over concrete. When carbonate bonded taconite tailings are used as a sub-base in conjunction with a bituminous surface, the paving costs obtained are comparable to conventional concrete/sub-base construction costs.

Table 12
Paving Cost, $/sq. yard

Secondary Road				Carbonate Bonding Cost Advantage
(1) 9 inch bituminous w/base	11.5	8 inch carbonate bonded layer	11.3	$0.2
(2) 12.5 inch bituminous w/base	13.0	6 inch bituminous w/6 inch carbonate bonded base	13.0	0.0

Table 12 -- Continued

Primary Road				Carbonate Bonding Cost Advantage
(1) 6 inch concrete w/6 inch base	13.7	6 inch carbonate bonded layer w/6 inch base	11.4	$2.3
(2) 4 inch concrete w/8 inch base	13.6	6 inch bituminous w/ 6 inch carbonate bonded base	13.0	0.6
(3) 6 inch concrete w/6 inch base	13.7	6 inch bituminous w/ 6 inch carbonate bonded base	13.0	0.7
(4) 8 inch concrete w/6 inch base	15.8	6 inch bituminous w/ 6 inch carbonate bonded base	13.0	2.8

Although the above comparisons are estimates of paving costs, the indication is that taconite tailings can be economically utilized as a road construction material. Not only does the cost of utilizing carbonate bonded taconite tailings as paving material compare favorably with conventional materials, but utilization of this waste material would minimize disposal (stockpiling) and reduce its harmful ecological effects.

APPENDIX

THEORETICAL CONSIDERATIONS OF CARBONATE BONDING

In the carbonate bonding process lime hydrate, water, and filler material are blended, compacted, and reacted with carbon dioxide to form a strong calcium carbonate crystal matrix. This reaction can be represented simply as follows:

$$CaO + CO_2 \longrightarrow CaCO_3 \qquad (1)$$

The relationship between the compressive strength of carbonate bonded materials and process operating variables is as yet not full understood. Prior experimentation on soils, clays, coal refuse, and sand indicates that compressive strength increases as:

1. The particle size of the fill material and lime hydrate decreases

2. An optimum water content is selected for each specific fill material

3. The external surface area of the fill material increases

4. The carbon dioxide partial pressure in the carbonating gas is balanced so that the rate of heat generation within the composite equals the rate of heat loss to the surrounding gas phase

5. The time of carbonation increases, and

6. The lime hydrate concentration increases

Decreasing the particle size (along with a wider particle size distribution) of the fill material decreases the porosity of the composite which is to be carbonate bonded. Decreasing the porosity yields a more dense composite and enhances the formation of a continuous calcite matrix. As the compressive strength of the composite is mainly a function of the continuity of the calcite crystal structure, a minimum porosity condition increases the strength of the carbonate bonded material.

As the surface area of the lime hydrate increases, its rate of solution in water is increased. This causes the carbon dioxide to react with a saturated lime hydrate solution and results in a rapid precipitation of a fine calcite crystal matrix. The rapid formation of a multitude of crystals enhances additional crystaline growth so that bridging and growth can occur between crystals with a resulting increase in strength.

In general, the greater the external specific surface area of the fill material, the greater will be the rugosity or roughness of the surface of the particles. This condition provides numerous bridging channels between particles for the growth of calcite crystals and increases the strength of the carbonate bonded material.

The effect of the partial pressure of carbon dioxide in the carbonating gas on the carbonation reaction is directly related to the gas phase mass transfer of carbon dioxide to the liquid film. Prior experimentation has shown that the rate of the carbonate bonding reaction is directly proportional to the partial pressure of carbon dioxide. Since the carbonate bonding reaction is highly exothermic, the heat released during this reaction can be controlled by varying the partial pressure of carbon dioxide in the gas phase. Depending upon the water content, the thermal characteristics and packing of the fill material, it is possible to crack the resulting carbonate bonded material by causing the reaction to occur too rapidly. Due to a high carbonation rate, sufficient heat is generated to produce steam within the interior of the composite. If the packing is too dense, rapid steam evolution from the carbonate bonded material is inhibited and can result in sufficient internal pressure to crack or rupture the composite. Consequently, the partial pressure of carbon dioxide must be optimized so that internal pressure cracks are not generated and the strength characteristics of the carbonate bonded material can be maintained.

A simplified model of carbonate bonding has been developed. The model considers that the progression of an interface separating a carbonate bonded zone from an unreacted zone in a slab of lime hydrate bearing material is controlled by the diffusion of CO_2 into the slab. That is, the carbonate bonding reaction (1), is assumed to be instantaneous and irreversible with no CO_2 beyond the moving interface. The model is shown in Figure 20. As seen, CO_2 (component A) is in contact with a slab of lime bearing material (component B, CaO) which is infinitely long and deep. The distance measured from the CO_2-solid interface (the slab surface) is represented by Z. Z'(t) designates a parallel interface separating a region of totally carbonate bonded material ($C_B = 0$ when $0 < Z \leq Z'(t)$) from a region having no CO_2 (component A). In the latter region, the concentration of CaO at time t is still equal to the concentration at time 0 ($C_B = C_B$ (0) when Z'(t) Z infinity). The concentration of CO_2 at Z = 0 is assumed to be constant and equal to C_A (0) whereas $C_A = 0$ at Z = Z'(t), since the carbonate bonding reaction is assumed instantaneous. The distance Z'(t) is a function of time (t) since the boundary between A and B advances into the slab as B is consumed in the reaction. The differential equation representing the diffusion of CO_2 into the slab is

$$\frac{\partial C_A}{\partial t} = \frac{D_{AS}\,\partial^2 C_A}{\partial Z^2} \qquad 0 < Z \leq Z'(t) \qquad (2)$$

where D_{AS} is the diffusivity of CO_2 in the slab.

The solution of equation (2) has the form:

$$\frac{C_A}{C_A(0)} = a_1 + a_2 \operatorname{erf}\left(\frac{Z}{\sqrt{4D_{AS}t}}\right) \qquad (3)$$

where a_1, a_2 are integration constants.

It can be shown that equation (3) can yield the movement of the carbonate bonded interface as a function of time. The resulting expression of $Z'(t)$ with time is:

$$Z' = \sqrt{4Kt} \qquad (4)$$

where K is an integration constant.

Thus the model predicts that the progression of the carbonate bonded interface will be related to the square root of time. It can also be shown that the average rate of diffusion of components A, $\bar{N}_A$, up to time T is:

$$\bar{N}_A = \frac{2C_A(0)}{\operatorname{erf}\sqrt{K/D_{AS}}}\sqrt{\frac{D_{AS}}{t}} \qquad (5)$$

This infers that the rate of diffusion of CO_2 is directly proportional to the concentration of the CO_2 in the reaction feed gas, $C_A(0)$. For a given reaction time t, the thickness of the carbonate bonded zone will also be directly proportional to $C_A(0)$.

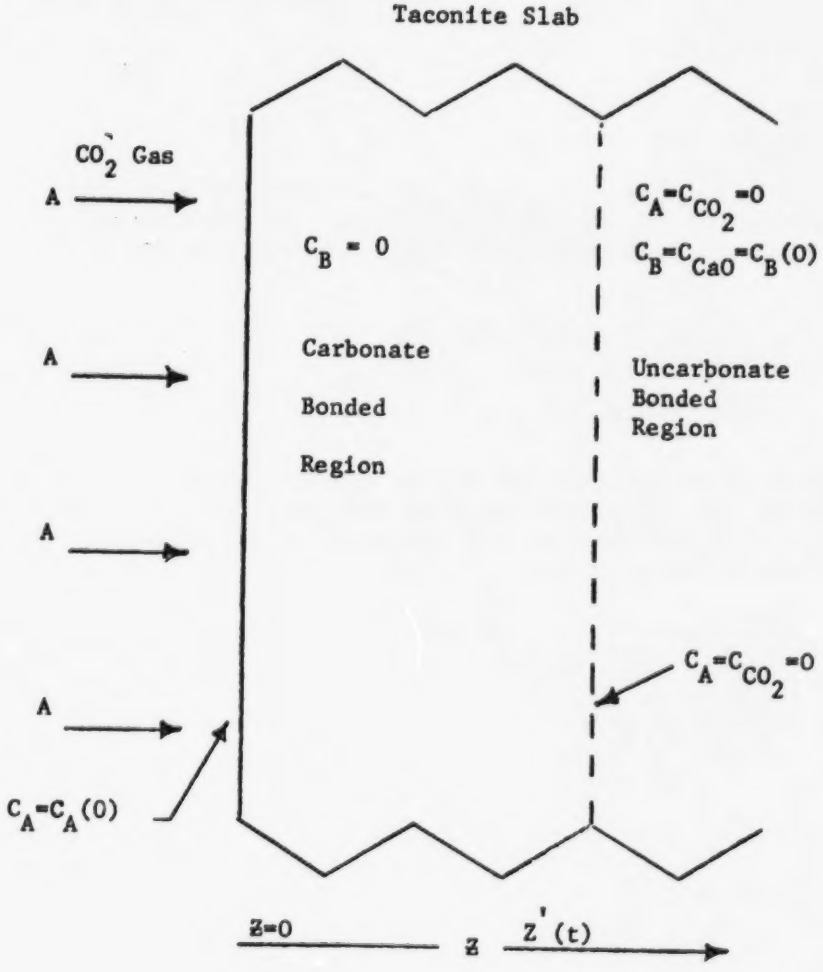


FIGURE 20. CARBONATE BONDING MODEL

DETERMINATION OF AIR PERMEABILITY

The air permeability of taconite tailings briquettes was determined using the apparatus schematically represented in Figure 21. The apparatus consists of a 5 cm I.D. by 53 cm high plexi-glass chamber on the bottom of which is cemented a taconite tailings briquette. The top of the chamber was sealed with a plexi-glass plate containing a pressure gauge. The chamber was pressurized with gas and the change in chamber pressure with time was measured to determine the permeability of the taconite tailings briquette. An initial chamber pressure of 1.4 kg/cm^2 (20 psig) was used. For an experimental run, the chamber pressure was allowed to decrease to a pressure of 0.07 kg/cm^2 (1 psig) before termination. Several tests were performed to determine the air permeability which was defined as the volumetric flow rate of air (m^3/hr) per cross-sectional flow area (m^2) per unit pressure driving force ($kg/m^2/m$).

The determination of air permeability is based on the fact that when a pressure difference exists across a porous solid, a flow of gas through the solid will occur. This is not diffusional flow in the usual sense but it can be described using the methods of diffusion. For the permeation of gas through a taconite tailings briquette, where the diameter of the capillaries is small and the gas velocity through the solid is small, flow will be streamline and can be described by Porseuille's law for a compressible fluid obeying the perfect gas law:

$$N = \frac{d^2 g}{32 u l R T} P_a (P_1 - P_2) \qquad (1)$$

where $P_a = (P_1 + P_2)/2$

To facilitate discussion, the following nomenclature will be used:

A	Area through which gas is flowing
d	Diameter of a capillary
g	Conversion factor
l	Length of capillary
N	Rate of diffusion
n	Moles
P	Pressure
P_1	Gas pressure in pressure vessel
P_2	Atmospheric pressure
P^o	Gas pressure in pressure vessel at time zero
P^a	$(P_1 + P_2)/2$
R	Universal gas constant
T	Absolute Temperature
t	Time
u	Viscosity
V	Volume of pressure vessel
v	Volume
Z	Height of Briquette

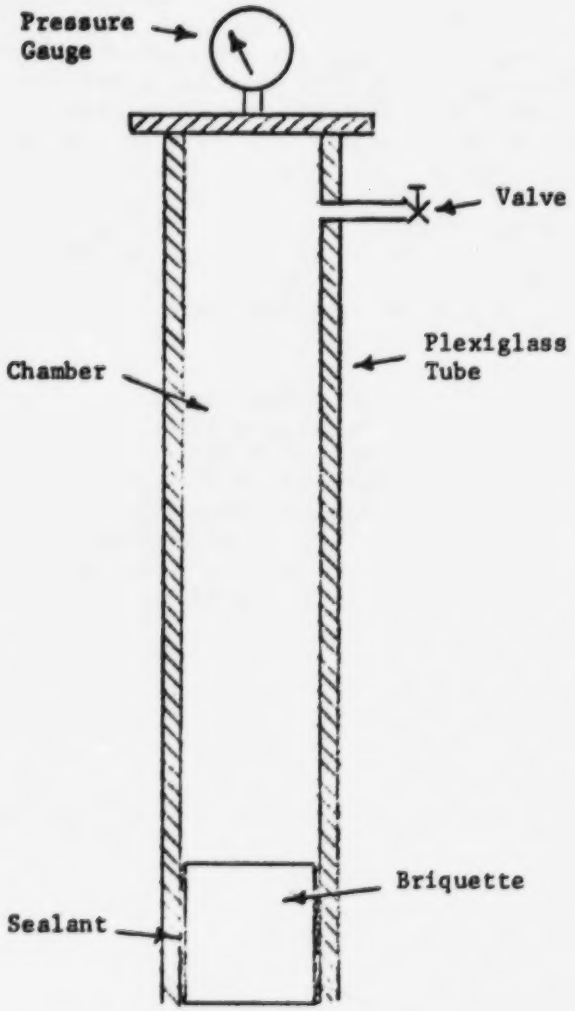


FIGURE 21. AIR PERMEABILITY APPARATUS

The perfect gas expression which relates the pressure, temperature, and volume of a perfect gas is expressed as

$$Pv = nRT \tag{2}$$

The experimental procedure used to determine the permeability of taconite tailings briquettes consisted of using a briquette as a plug in a pressure vessel (Figure 21) and determining the pressure within the vessel as a function of time. This is an unsteady state operation in which the pressure driving force is continually changing with time; therefore, a mass balance on the gas contained in the vessel yields

$$\frac{dn}{dt} = -NA \tag{3}$$

where A is the area through which gas flow is occurring

Expressions (1) to (3) form the basis of the mathematical treatment required to determine permeability. Substituting equation (1) into (3) yields

$$\frac{dn}{dt} = -\frac{d^2 gA}{32\ ulRT} \quad P_a\ (P_1 - P_2) \tag{4}$$

Taking the differential of the ideal gas law, equation (2), with dv = 0 results in $dn = Vdp_1/RT$ and substituting this expression into (4) yields

$$\frac{dP_1}{dt} = -K\,\frac{P_1 + P_2}{2}\ (P_1 - P_2) \tag{5}$$

where $K = A\ d^2 g/(32\ Vul)$

Rearranging equation (5) results in the following expression relating the pressure within the vessel P_1 to time t

$$\int_{P_o}^{P_1} \frac{dP_1}{P_2^{\,2} - P_1^{\,2}} = \frac{K}{2} \int_0^t dt \tag{6}$$

where P_o is the initial pressure in the vessel at time t = 0.

Integrating the above expression between the indicated limits yields the following relationship between the chamber pressure P_1 and t:

$$\ln \frac{(P_2+P_1)/(P_2-P_1)}{(P_2+P_1)/(P_2-P_1)} = KP_2t \qquad (7)$$

Expression (7) is used to determine K since experimentally P_1 is known as a function of time. The parameter K is determined as the slope of

$$(P_2 + P_o/P_2 - P_o)/(P_2 + P_1/P_2 - P_1) \text{ vs } t$$

By definition, the permeability of a porous solid is the rate of diffusion per unit pressure gradient across the solid. The permeability P can be defined using the following expression for which P has the units of $m^3/hr - m^2 - (kg/m^2/m)$ and z is the depth of the porous solid in the direction of flow.

$$P = (N\ RT/P_a)/(P_1 - P_2/z) \qquad (8)$$

Substituting expression (1) into (8) yields a relationship between the parameter K and permeability:

$$P = \frac{KVz}{A} \qquad (9)$$

Since K is known from (7) and V, z, and A are known, the permeability can be established using expression (9).

DETERMINATION OF WATER PERMEABILITY

Water permeability is the mass flow rate of water per cross-sectional flow area per unit pressure driving force. The water permeability of taconite tailings was determined using the apparatus shown in Figure 22. This apparatus consists of a 5 cm I.D. by 61 cm high plexi-glass primary chamber sealed on top with a plexi-glass plate containing a valve and on the bottom with a taconite tailings briquette. An additional chamber was attached to the primary chamber and located beneath the briquette to collect the water permeating through the briquette and to prevent unrealistic permeation rates due to convective air flows about the exposed surface of the briquette.

In addition, water permeating through carbonate bonded taconite tailings will probably enter into surroundings which will normally be saturated with water vapor. The lower chamber, therefore, provides a water vapor saturated atmosphere to better simulate actual conditions and provide more meaningful results. The lower chamber contains a small hole on its side to vent evaporated water and to prevent a buildup of pressure.

The water permeability test was conducted by initially filling the primary chamber with water to a level of 48 cm and, on a daily basis, measuring the amount of water lost due to permeation. After the quantity of water loss was determined, this amount was added back into the primary chamber to maintain a constant pressure driving force.

This test was run for 35 days and an average rate of water permeation determined. For all practical purposes this test was run on a steady state basis in which the water pressure driving force was constant; consequently, the water permeability of taconite tailings can be directly calculated since the flow area of the briquette, the thickness of the briquette, the constant water pressure driving force, and the average rate of water permeation are known.

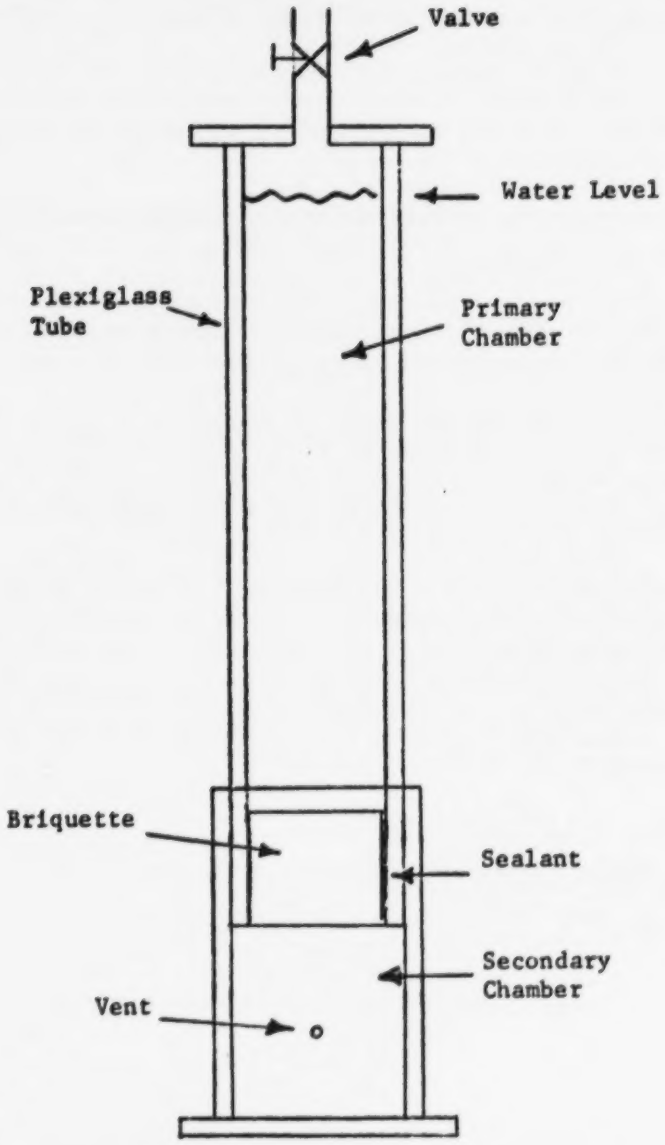


FIGURE 22. WATER PERMEABILITY APPARATUS

FREEZE-THAW TEST

The freeze-thaw test was based on the ASTM test C290-67 entitled "Standard Method of Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water". The freeze-thaw,as modified for this study, is as follows.

Freeze-thaw experiments were conducted using a refrigerator in which the refrigeration area was at 2 to 5°C and the freezing compartment at -18 to -16°C. To initiate the freeze-thaw test, eight briquettes each of Ohio Super Spray, National Hydrate, Pfizer Spray with taconite briquettes were soaked in water for one hour and then placed in the freezing compartment for four hours. The freeze-thaw test required a rigid schedule in order to make the results meaningful. The schedule was as follows:

	Time	Event
	9:00 a.m.	Remove from freezing compartment. Place in thawing water.
Complete Cycle	10:00 a.m.	Remove from thaw water. Place in freezing compartment.
	2:00 p.m.	Remove from freezing compartment. Place in thawing water.
Complete Cycle	3:00 p.m.	Remove from thawing water. Place in freezing compartment.
	7:00 p.m.	Remove from freezing compartment. Place in thawing water.
Complete Cycle	8:00 p.m.	Remove from thawing water. Place in freezing compartment.

A freeze-thaw cycle consisted of one thawing operation and one freezing operation. After five of these cycles, one of each of the three different kinds of briquettes was removed from the system and allowed to air dry for one to two days. The compressive strength of these samples was then determined. This procedure was repeated at every five cycles up to forty cycles. The data obtained was the compressive strength as a function of the number of freeze-thaw cycles for each kind of briquette.